EPA   PROPOSED METHODS FOR STACK EMISSIONS MEASUREMENT OF CO, O$_2$, THC, HCl, AND METALS AT HAZARDOUS WASTE INCINERATORS

VOLUME VI OF THE HAZARDOUS WASTE INCINERATION GUIDANCE SERIES

HAZARDOUS WASTE INCINERATION GUIDANCE SERIES

Volume I Guidance Manual for Hazardous Waste Incinerator Permits, Mitre Corp., 1983. NTIS No. PB 84 100577.

Volume II Guidance on Setting Permit Conditions and Reporting Trial Burn Results, EPA/625/6-89/019. USEPA, January 1989.

Volume III Hazardous Waste Incineration Measurement Guidance Manual, EPA/625/6-89/021, USEPA, 1989.

Volume IV Guidance on Metals and Hydrogen Chloride Controls for Hazardous Waste Incinerators, USEPA, August 1989.

Volume V Guidance on PIC Controls for Hazardous Waste Incinerator, USEPA, April 1989.

Volume VI Proposed Methods for Stack Emissions Measurement for CO, O_2, THC, HCl, and Meta's at Hazardous Waste Incinerators, USEPA, November 1989.

NOTE: Volumes II and III are available from EPA, ORD, Cincinnati, Ohio 45268 (phone 513-569-7562) and Volumes IV through VI from EPA, OSW, Washington, DC 20460 (phone 202-382-3000).

PROPOSED METHODS FOR
STACK EMISSIONS MEASUREMENT
FOR CO, O_2, THC, HCl, AND METALS
AT HAZARDOUS WASTE INCINERATORS

DRAFT FINAL REPORT

VOLUME VI OF THE HAZARDOUS WASTE
INCINERATION GUIDANCE SERIES

U.S. Environmental Protection Agency
Office of Solid Waste
Waste Treatment Branch
401 M Street, SW
Washington, DC 20460
Work Assignment Manager: Mr. Shiva Garg

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SECTION 1.0

INTRODUCTION

The hazardous waste incinerator rules now in effect at 40 CFR Part 264, Subpart 0 establish three performance standards. Incinerators burning hazardous waste must achieve a destruction and removal efficiency (DRE) of 99.99 percent for each Principal Organic Hazardous Constituent (POHC) designated for each waste feed. Metals emissions are controlled indirectly by a particulate matter emissions limit of 180 milligrams per dry standard cubic meter (or 0.08 gr/dscf). Finally, hydrogen chloride emissions are controlled by a standard that requires emissions to be reduced by 99 percent if emissions exceed 4 lb/h.

EPA is proposing to amend the hazardous waste incinerator regulations to provide improved control of toxic metals emissions, hydrogen chloride emissions, and residual organic emissions. The proposal will establish risk-based emission limits for individual toxic metals listed in Appendix VIII of 40 CFR Part 261. The limits would be back-calculated from ambient levels that EPA believes pose acceptable health risk. To reduce the burden to the applicant and permitting officials, EPA has developed conservative screening limits. If the screening limits are not exceeded, emissions do not pose unacceptable risk. If the screening limits are exceeded, however, site-specific dispersion analysis would be required to demonstrate that emissions would not result in exceeding acceptable ambient levels. EPA is proposing to regulate HCl under the same risk-based approach proposed for metals.

The proposal will also limit emissions of products of incomplete combustion (PICs), that may be present at levels that could pose significant health risk. The complete combustion of all hydrocarbons to produce only water and

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carbon dioxide is theoretical and could occur only under ideal conditions. Real-world combustion systems (e.g., incinerators, fossil fuel steam generators, diesel engines), however, virtually always produce PICs, some of which have been determined to be highly toxic. EPA believes that requiring incinerators to operate at high combustion efficiency is a prudent approach to minimize the potential health risk posed by PIC emissions. Given that stack gas carbon monoxide (CO) is a conventional indicator of combustion efficiency and a conservative indicator of combustion upsets (i.e., poor combustion conditions), the proposed rule would limit CO emissions to a *de minimis* level that ensures high combustion efficiency and low unburned hydrocarbon emissions. In cases where the *de minimis* CO limit is exceeded, the owner or operator would be required to demonstrate that higher CO levels would not result in hydrocarbon emissions that could pose significant health risk or to comply with a *de minimis* level consistent with good operating practices. Conservative, risk-based emission limits were developed for hydrocarbon emissions similar to those for metals and HCl.

This document discusses proposed measurement methods that will be required to implement the proposed amendments to the incinerator rules. Section 2 presents a summary of these measurement requirements. Sections 3 through 7 discuss the methods. The specific methods discussed are appended.

SECTION 2.0

SUMMARY OF MEASUREMENT REQUIREMENTS

The proposed amendments to CFR Part 264, Subpart O will provide limits for toxic metals, hydrogen chloride (HCl), and carbon monoxide (CO) as a surrogate for products of incomplete combustion (PIC). A variety of measurements will be required to determine compliance with feed and emission rate screening limits and to provide data necessary for corrections applied to the CO emission levels. These measurement requirements are summarized in Table 2.1 and discussed below. The proposed amendments should be referred to for a description of the specific limitations.

Dual-level CO monitors will be required to measure both high and low concentrations accurately for calculation of the hourly rolling average and for the peak and lower level limit used in the alternate format. A single-level monitor is adequate for the continuous oxygen measurements. The measurement ranges required for these monitors are from a low value of zero to a high value as follows:

1.   For the low range CO measurement, the high level value is set between 1.5 times the permit limit and a span value of 200 ppm for Tier I and 2 times the permit limit for Tier II.

2.   For the high range CO measurements, except for Tier II using the alternate format, the high level value is set between 2000 ppm as a minimum and a span value of 3000 ppm.

3.   For the high range CO measurement under Tier II using the alternate format, the high level value is set at a span value of 1.1 times the permitted peak value.

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TABLE 2.1. SUMMARY OF MEASUREMENT REQUIREMENTS

Proposed paragraph in §264.343	Limitation	Measurements required
(b)(1)(i)	Tier I CO limit	Continuous CO concentration Continuous oxygen concentration (for rolling average format) Oxygen level during trial burn (for alternate format) Moisture level during trial burn (if CO measured as wet gas)
(b)(1)(ii)	Tier II CO limit and THC screening or de minimis limits	Same as Tier I plus the maximum hourly average total hydrocarbon concentration during the trial burn Standard, dry stack gas flow rate
(d)(2)	Metals* feed rate screening limits	Concentration of specified metals in the waste Waste feed rate
(d)(3)	Metals* emissions rate screening limits	Stack emission rates of specified metals Standard, dry stack gas flow rate
(e)(2)	HCl feed rate screening limits	Concentration of total chlorine in the waste Waste feed rate
(e)(3)	HCl emission rate screening limits	Stack emission rate of HCl Standard, dry stack gas flow rate

* Metals of concern are: arsenic, cadmium, chromium, beryllium, antimony, barium, lead, mercury, silver, and thallium.

4. For oxygen, the high level value is set between 1.5 times the highest level measured during the trial burn and a span value of 25 percent.

Typical measurement requirements for oxygen and moisture trial burn levels will be about 5 to 15 percent for oxygen and up to about 60 percent for moisture.

The THC, metals, and chlorine measurements need to provide accurate concentration data that correspond to the range of feed rate and emission rate screening values in the proposed regulations. These concentration values are shown on Table 2.2. The low ends of the concentration ranges on Table 2.2 were calculated by matching the smallest compound rates in the screening tables with the high end of the range of typical waste feed rate and stack gas flow rates for hazardous waste incinerators. The high concentrations correspond to the highest compound rates and lowest waste feed and stack gas flow rates. The waste feed rate and stack gas flow rate ranges were derived from data on eight hazardous waste incinerators found in the EPA Report (EPA 600/2-84-181d) entitled, "Performance Evaluation of Full Scale Hazardous Waste Incinerators Volume 4." The range of waste feed rate and stack gas flow rates are 1.7×10^{-5} to 6.7×10^{-4} mg/s, and 1,000 to 30,000 dscf/m, respectively. It is very unlikely that measurements near either end of the ranges will be needed. The low end represents screening values that correspond to short stacks and high waste feed or stack gas flow rates, an unlikely combination. The converse is true at the high end of the ranges.

The stack gas flow rate and waste feed rate measurements shown on Table 2.1 are necessary to convert concentration values measured by the methods in this document to emission and waste feed rates. These measurements are the same as required under the existing regulations and are not covered in this document.

Sampling methods for waste are also required under the existing regulations and are not covered in this document.

TABLE 2.2.   RANGE OF MEASUREMENT LEVELS FOR THC, METALS, AND HCl

Compound	Waste concentration for feed rate limits (µg/g)	Stack concentration and sampling train mass for emission rate limits	
		Conc. (µg/dscf or as noted)	Mass (mg)[a]
THC	–	1 ppm – 4%	
Arsenic	$0.1 - 4 \times 10^3$	$0.06 - 4 \times 10^3$	$0.004 - 3 \times 10^2$
Cadmium	$0.4 - 7 \times 10^3$	$0.1 - 1 \times 10^4$	$0.006 - 6 \times 10^2$
Chromium[b]	$0.07 - 1 \times 10^3$	$0.02 - 1 \times 10^3$	$0.001 - 6 \times 10^1$
Beryllium	$3 - 7 \times 10^4$	$1 - 6 \times 10^3$	$0.06 - 4 \times 10^3$
Antimony	$20 - 5 \times 10^5$	$8 - 5 \times 10^5$	$0.5 - 3 \times 10^4$
Barium	$4,000 - 7 \times 10^7$	$1,000 - 6 \times 10^7$	$60 - 4 \times 10^6$
Lead	$7 - 1 \times 10^5$	$2 - 2 \times 10^5$	$0.1 - 1 \times 10^4$
Mercury	$100 - 4 \times 10^6$	$60 - 4 \times 10^6$	$4 - 3 \times 10^5$
Silver	$200 - 5 \times 10^6$	$80 - 5 \times 10^6$	$5 - 3 \times 10^5$
Thallium	$20 - 5 \times 10^5$	$8 - 5 \times 10^5$	$0.5 - 3 \times 10^4$
Total chlorine	$100 - 6 \times 10^5$	–	–
HCl	–	$50 - 6 \times 10^5$	$3 - 4 \times 10^4$

[a] Based on 60-ft³ sample volume (approximately 0.5 cfm for 2 h).

[b] Chromium can be measured as either total chromium or chromium(VI).

SECTION 3.0

CONTINUOUS MEASUREMENT OF CARBON MONOXIDE AND OXYGEN

The "method" for continuous emission monitoring of CO is in the format of a performance specification. The performance specification provides specific performance criteria that must be met by the monitoring system but does not specify the type of instrument which must be used nor provide specific design criteria for the monitoring system. This format is chosen for three reasons. First, the most important evaluation criteria for a continuous emission monitoring system is how the system performs; i.e., does the system provide accurate, precise, and reliable results. Second, many different types of CO analyzers exist and the instrument technology is constantly changing. Specification of a specific method (i.e., a specific instrument) does not allow flexibility to the owner/operator in choosing the monitoring system that best suits their needs and will perform best for their application. The development of specific methods which specify design criteria for all acceptable monitoring systems would be an insurmountable task. Third, this approach has previously been successfully used by the U.S. EPA in specifying monitoring requirements for sulfur dioxide and nitrogen oxides from stationary sources of air pollutants (Performance Specification 2, 40 CFR 60, Appendix B).

The CO limits for hazardous waste incinerators require that the CO concentration be normalized to a constant stack gas oxygen level (i.e., corrected for the amount of dilution by excess or "diluent" air); the normalization used is 7 percent oxygen. This normalization requires measurement of the oxygen concentration, and, depending upon the permit format, continuous measurement of oxygen may be required. Therefore, the performance specification includes performance standards for oxygen monitors.

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The performance specification is used to evaluate the entire continuous emission monitoring system's (CEMS) performance just after its initial installation, calibration, and snakedown period to determine if the CEMS performs in an acceptable manner. The performance specification does not include procedures for routinely (i.e., daily, weekly, monthly, etc.) assessing monitor performance and calibration. Calibration requirements are addressed in Section 3.2. A separate quality assurance program should be established to assure that acceptable calibration and performance is maintained. It is appropriate for the performance specification (or selected parts of the specification) to be used periodically (e.g., annually) as part of the QA program. Following are general guidelines for a QA program:

1. Conduct a daily calibration check for each monitor. Adjust the calibration if the check indicates the instrument's calibration drift exceeds the specification established in Appendix A.

2. Conduct a daily system audit. During the audit, review the calibration check data, inspect the recording system, inspect the control panel warning lights, and inspect the sample transport/interface system (e.g., flowmeters, filters), as appropriate.

3. Conduct a quarterly calibration error test at the span midpoint.

4. Repeat the entire performance specification test every second year.

The remainder of this section discusses types of monitoring systems and data reporting and calibration. Appendix A contains the performance specifications.

3.1 TYPES OF CARBON MONOXIDE AND OXYGEN CONTINUOUS EMISSION MONITORING SYSTEMS

CO and oxygen monitors can be classified according to the analytical methods employed; current methods employed include:

For carbon monoxide--

    a.   Nondispersive infrared spectrometry (NDIR)

    b.   Gas filter correlation nondispersive infrared spectrometry (GFC)

    c.   Electroanalytical methods (catalytic oxidation, polarographic)

    d.   Gas chromatography (GC), and

    e.   Fourier transform infrared spectrometry (FT-IR)

For oxygen--

    a.   Electroanalytical methods (catalytic oxidation, polarographic, and paramagnetic), and

    b.   Gas chromatography

A CEMS system also can be designed to monitor a flue gas using any one of three basic approaches. These are:

1.   Extractive--the sample gas is extracted from the flue, conditioned, and transported to a remote analyzer.

2.   In situ--the sensing portion of the analyzer is physically located in the flue gas stream and the flue gas flows through or over the sensor.

3.   Cross-stack--the sensing portion of the analyzer is mounted on the duct and the analyzer projects a sensing beam across the stack through the flue gas.

With the exception of gas chromatography, all of these types of analyzers and the three basic approaches can potentially meet the criteria established in

the performance specification. Gas chromatography cannot meet the requirements because the specification defines a continuous emission monitor as a device in which 'the sample to be analyzed passes the measurement section of the analyzer without interruption and which evaluates the detector response to the sample at least once each 15 s." A gas chromatographic system does not meet these criteria.

The theories of operation for the different analyzer types, the evaluation criteria for choosing a system/analyzer type, and the system design details are too complex and lengthy to discuss in this document. However, several documents which discuss this information, in general, for CEMS are publicly available. These are:

- "Continuous Air Pollution Source Monitoring Systems," J. Jahnke, EPA 625/6-79-005, June 1979.

- Gaseous continuous Emission Monitoring Systems--Performance Specification Guidelines for SO_2, NO_x, CO_2, O_2, and TRS. U.S. EPA, EPA-450/3-82-026, October 1982, NTIS PB 83-161646.

3.2 REPORTING AND CALIBRATION

This section addresses continuing reporting and calibration. Consistent reporting is necessary to provide a clear continuing measure of compliance with the proposed regulations, and routine calibration ensures continuing data quality. The paragraphs below detail these recommended reporting and calibration requirements.

(a) All continuous monitoring systems should be installed and operational prior to conducting the trial burn. Verification of operational status should include completion of the manufacturer's written requirements or recommendations for installation, operation, and calibration of the device.

(b) Within 120 days prior to or during a trial burn, a continuous monitoring system performance evaluation should be conducted and a written report of the results prepared. (It is highly recommended that the performance tests be conducted prior to the trial burn to verify that the monitors are operating properly during the trial burn.) These continuous monitoring system performance evaluations should be conducted in accordance with the requirements and procedures contained in Appendix A of this document.

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(c) The zero (or low level value between 0 and 20 percent of full scale measurement range) and span (50 to 100 percent of full scale measurement range) calibration drifts should be checked at least once daily in accordance with a written procedure. The zero and span should, as a minimum, be adjusted whenever the 24-h zero drift or 24-h span drift exceeds two times the limits of the performance specification. The system must allow the amount of excess zero and span drift measured at the 24-h interval checks to be recorded and quantified.

(d)   Except during calibration checks recommended under paragraph (c) above, all continuous monitoring systems should be operated continuously when hazardous waste is incinerated and should meet minimum frequency of operation requirements as follows:

(1) Systems for measuring CO emissions should complete a minimum of one cycle of sampling and analyzing for each successive 15-s period and one cycle of data recording for each successive 1-min period. Both the 1-min average and the most recent 60-min average are calculated as an arithmetic average (as follows):

$$Avg = \frac{1}{n} \sum_{i=1}^{n} X_i$$

where: n = number of observations
          X_i = individual observations

(2)   Systems for measuring oxygen for correction of CO emission concentrations should complete a minimum of one cycle of operation (sampling, analyzing, and data recording) each successive 15-min period.

(e) All data from CO continuous monitoring systems should be reduced to 1-min averages for recording. For Tier I and Tier II rolling average permit formats, the 1-min averages should be used to calculate and record a 1-h rolling average at 1-min intervals. The waste feed cut-off mechanism should be activated by the 1-h rolling average. For alternate Type B permit formats,

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1-min averages shall be recorded. However, the clock-timer used to measure the accumulated time above the permitted limit and to activate waste feed cut-off should interact with the 15-s sample/analyze cycle of the CO monitor. Data recorded during zero and span calibration checks should not be included in the data averages computed under this paragraph.

All data should be recorded in the reduced units applicable to the permit limit (i.e., CO normalized to 7 percent O_2). Where O_2 is required to be continuously monitored, the value used to calculate the normalized CO concentration must be measured and entered into the calculation at least every 15 min. The continuous correction to 7 percent oxygen in the stack gas is made according to the formula:

$$CO_c = CO_m \times \frac{14}{21 - Y}$$

where CO_c is the corrected concentration of CO in the stack gas, CO_m is the measured CO concentration, and Y is the measured oxygen concentration on a dry basis in the stack. Oxygen must be measured at the same stack location that CO is measured.

When oxygen enriched air is used for incineration, a different correction factor is necessary to account for the reduced volume of gas. The corrected CO concentration for the oxygen enriched system can be calculated as follows:

$$CO_c = CO_m \times \frac{14}{E - Y}$$

where E is the oxygen concentration in the enriched combustion air (e.g., 30 percent), and Y is the measured oxygen concentration in the dry stack gas. When the enriched oxygen concentration, E, is not known or is anticipated to vary, as in cases of significant air inleakage or variable combustion air supply, alternative correction factors based on the measured CO_2 concentrations in the stack gas are available in the literature.[1]

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[1] Garg, S., and Castaldini C., "Derivation of oxygen correction factors for oxygen enriched incinerators," *JAPCA Journal*, 39, pp. 1462-5, November 1989.

SECTION 4.0

METHODS FOR MOISTURE AND OXYGEN MEASUREMENTS

If the CO and/or the oxygen continuous emission monitors measure the effluent gas on a wet basis, then moisture measurements will be required during the trial burn and at intervals specified by the permit writer thereafter. Moisture measurements are made using Reference Method 4--Determination of Moisture Content in Stack Gas, or in conjunction with Reference Method 5--Determination of Particulate Emissions from Stationary Sources; both methods are published in 40 CFR 60, Appendix A.

When the alternate time above a CO limit format is used, oxygen measurements need not be continuous for the life of the permit. Rather, they are performed annually or on a more frequent basis as specified in the permit. For these intermittent measurements, Reference Method 3--Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight (40 CFR 60) is the method used. Method 3 presents several optional procedures. The method to be used is single-point, integrated sampling (multipoint integrated sampling at the permit applicant's option) with analysis for oxygen by ORSAT. Alternatively, Reference Method 3A--Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure) may be used.

Copies of these methods are in Appendix B of this document.

SECTION 5.0

METHOD FOR TOTAL HYDROCARBON MEASUREMENT

Measurement of total hydrocarbon (THC) concentration in incinerator stack gases will be required during trial burns if the proposed Tier II Carbon Monoxide (CO) limit is used. The THC is used as a surrogate for total organic emissions. The method selected is a modification of EPA Method 25A (48 FR 37595, 8/18/83) which uses a flame ionization detector (FID). The modification specifies the temperatures that need to be maintained for a heated system and the specification of a sample gas conditioning system for moisture removal in an unheated system.

Ideally, a heated THC monitoring system would be used. In a heated THC system the temperature of the sample gas is maintained well above the moisture dew point temperature, above 150°C (300°F), throughout the entire system (i.e., the sample line, particulate matter filter, sample pump, and analyzer). The advantage of the heated THC system is that condensation of the organic compounds contained in the sample gas is minimized within the sample transport system. Typical unheated systems use condensate traps to "condition" the sample gas by condensing moisture (and organic compounds). With this unheated method, more semivolatile organic compounds are condensed and water-soluble volatile compounds may also be removed from the sample gas with the moisture. These compounds would not reach the analyzer and be detected. Thus, the THC readings from the unheated monitoring system are less than the

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actual quantity of total organic emissions. Several studies[1,2,3] have been done where parallel measurements were made with both the heated and unheated systems, and it was found that measurement readings by a hot system are higher than those by a cold system by up to a factor of 5.

The disadvantage of a heated system is that the sample handling system is more complex because all components must be heated to ensure that condensation does not occur anywhere in the system. This complexity may result in operating and maintenance problems. Currently, the ability to operate and maintain a heated THC system over an extended period of time has not been adequately demonstrated, although such systems have been routinely used for short periods of time during trial burns and research tests for several years.[4,5,6]

A recent survey[7] conducted by EPA/OSW indicates that six hazardous waste incinerators currently monitor THC on a continuous basis using FID monitors, but none of them uses a fully heated system. The monitoring systems currently being employed are varied and typically utilize a sample conditioning system which cools the sample gas to remove moisture and prevent condensation within the analyzer. One facility bubbles the sample gas through a water column as a part of sample conditioning. Three facilities use heated sample lines. Since

[1] EPA, Measurement of Particulates, Metals, and Organics at a Hazardous Waste Incinerator, November 1988, NTIS No. PB89-230668.
[2] Midwest Research Institute, "Draft Pretest Report--Ash Grove Precalcines Kiln," EPA Contract No. 68-01-7287, October 17, 1989.
[3] Entropy Environmentalists, Inc, "Evaluation of CO and THC Analyzers for Waste Incinerator Emission Measurement," Draft Report, EPA Contract No. 68-02-4442, October 1989.
[4] Trenholm, A., P. Gorman, and G. Jungclaus, "Performance Evaluation of Full-Scale Hazardous Waste Incinerators. Volume 2 - Incinerator Performance Results," EPA-600/2-84-181b, PB85-129518, November 1984.
[5] Hlustick, Dwight, Memo to Shiva Garg, "Summary of THC Measurements in Cement Kilns," October 20, 1988.
[6] Shamat, Nadim, Letter to Eugene Crumpler and attached progress report on THC analyzer evaluation study, October 3, 1989.
[7] Trenholm, A., and Williams, D., "THC Monitor Survey," Draft Final Report, EPA Contract No. 68-01-7287, MRI, June 30, 1989.

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there are no requirements to monitor THC thus far and no specifications for the monitoring systems were provided, such variations are not surprising.

The proposed regulations for sewage sludge incinerators[a] mandate the use of a heated THC system. In order to validate the heated THC system, the EPA, Office of Water, in a cooperative effort with the Metropolitan Waste Control Commission in St. Paul, Minnesota, has been operating and monitoring the performance and availability of a heated THC system; and the results, thus far after 6 months' usage, have found no problems with the heated THC monitoring system.[6]

As such, while the EPA recommends and encourages the use of heated systems, it does not mandate its use because of lack of available use experience. An alternative specification of an unheated monitoring system has been provided. In such a system, however, the potential for removal of some of the organic compounds from the sample gas during conditioning is of concern. Consequently, some criteria must be established for the conditioning system.

The unheated THC monitoring method requires the moisture removal device in the sample conditioning system to be maintained at a temperature between 5°C (40°F) and 18°C (64°F). The lower bound temperature has been specified for three reasons. First, during EPA's survey, several systems utilizing a chiller/condensor operating at or above this temperature were identified. Reliable operation of these systems has been demonstrated. Second, allowing the sample gas temperature to be lowered to 5°C to remove moisture effectively allows the remainder of the sample transport system to be operated at ambient temperature; if a chiller/condensor is used to condense the moisture from the gas stream at 5°C, then condensation within the remainder of the sample transport/analysis system at ambient temperatures will not be a problem. If, for example, a minimum allowable temperature of 20°C (68°F) was specified, then the entire conditioning/sample transport system would need to be maintained above this temperature to prevent condensation within the system. This specification would effectively require the entire system to be heated since

a   Sewage Sludge Incineration Proposed Rule, *Federal Register*, February 6, 1989.

operating at ambient temperatures would not ensure against further condensation. Third, at 5°C, the saturated moisture concentration of the gas stream will be about 0.8 percent. Several vendors of FID instruments contacted indicated that the moisture content of the gas delivered to the FID should be less than 2 to 5 percent; at 5°C, the moisture content is well below this level. The upper bound temperature is specified to ensure sufficient moisture removal for reliable operation of the monitor. At 18°C, the moisture content is about 2 percent.

Different techniques for removal of moisture from the sampling stream are available to the user, and the user should choose the technique(s) best suited for their application. Techniques available generally include some form of chiller/condensors. Scrubbers which purge the sample gas through water or an alkaline solution are not recommended as part of the conditioning system because of the potential for absorption of organic compounds. An alternative approach is the use of dilution air to reduce the dewpoint of the sample gas; obviously, the use of dilution air also decreases the THC concentration. This approach is not recommended since the concentration of organic compounds in the sample gas is anticipated to be low (< 100 ppm) and dilution will further decrease the concentration to levels near the detection limit (e.g., a 10:1 dilution will reduce an 80-ppm measurement to 8 ppm).

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SECTION 6.0

CHLORIDE MEASUREMENTS

This section addresses measurement of HCl in stack emissions and determination of the chlorine content of waste.

6.1 HCl EMISSION MEASUREMENTS

Hydrochloric acid (HCl) emissions are currently measured using a CEM or manual methods consisting of a collection train and/or analytical procedure. Two collection trains employed for the manual collection of an HCl sample are midget impingers or, most frequently, the back half of the EPA Method 5. The back half of a metals collection train can also be used. The HCl sample is recovered from the condensate and impingers which contain a trapping solution. The analysis on the chloride samples can be performed using one of a variety of chloride procedures; however, ion chromatography is the recommended method.

6.1.1 General Considerations

There are several assumptions made when sampling emissions for HCl. The analytical methods that are employed respond to the chloride ion. Any organic halide, being nonionic, will therefore not interfere. The assumption is therefore made that a sampling train containing a filter will collect all of the inorganic chlorides on the filter and pass HCl to be collected in the impingers. This assumption is reasonable for most wastes since only metallic halides such as mercury, arsenic, and antimony are not expected to be volatile at filter temperatures and consequently will not pass the heated filter.

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The analytical methods that have been employed for chloride analysis are generally referred to as interference free. This statement is made because many of the methods were developed for surface water analysis in which large quantities of bromine, iodine, and cyanides are generally not found. These ions generally do not cause a problem for the recommended ion chromatography method. However, it appears probable that some waste may contain high levels of these ions, in which case the other chloride methods would be positively biased. From the standpoint of controlling chloride emissions, this may be unacceptable for regulatory tests since the reported value would always be higher than the actual value.

6.1.2 Discussion of Sampling Methods

The HCl emissions are normally sampled by extracting a gas sample from the stack and absorbing the HCl in an absorbent. The sampling train consists of a Teflon mat particulate filter, the absorption solution, and a provision of measuring the sampled gas volume. The EPA Method 5 train, an EPA Method 5 train modified for metals, or a specific impinger train have all been employed. The M5 trains are normally used when HCl is to be collected in addition to sampling for particulates or metals. If sampling is to be performed for only HCl, then a specific impinger train is employed. For sampling HCl using the M5 as described in the *Federal Register*, the procedures are followed except that the water in the impingers is replaced with an adsorbing solution. A draft EPA method for HCl sampling is in Appendix D.

A solution of sodium or potassium hydroxide has frequently been used to absorb the HCl. This approach has been satisfactory except that the solution also absorbs the other acid gases contained in the sample including carbon dioxide (CO_2). The use of the hydroxide solution therefore requires that a correction be applied to the sample volume for the gases that were removed before the gas volume meter in the sampling stream. This correction may be avoided by substituting other solutions for the hydroxide. There is a lack of consensus on the impinger reagent most appropriate for collection of HCl. Sodium carbonate solution has been recommended, since this reagent will not absorb CO_2. There is evidence to suggest that caustic reagent is not

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necessary, and that HCl is efficiently trapped in any aqueous medium. If this is true, then distilled water (e.g., ASTM Type II reagent water) may be the reagent of choice for collection of HCl. The draft method in Appendix C recommends dilute acid solutions in the second and third impingers with a dilute caustic solution in the fourth impinger.

6.1.3 Discussion of Analysis Methods

A number of analytical methods have been employed to analyze the impinger catch for HCl. These methods include the automated ferricyanide colorimetric Methods 9250 and 9251 and the titrimetric Method 9252 from SW-846, ion chromatography ASTM Method D-4327-84 and EPA Method for Chemical Analysis of Water and Wastes, and Method 300.0.

Ion chromatography (IC) is the preferred method. The cost per run using IC is considerably greater than the colorimetric of titrimetric procedures; however, IC provides the only convenient method of quantitating the individual halogens. Since each run measures a number of ions, the cost per ion becomes competitive when each must be measured. Because of the greater detail provided, the ASTM D-4327-84 procedure is recommended over Method 300.0. A draft EPA method for ion chromatography analysis of HCl is in Appendix D.

The other methods mentioned above may be suitable in some circumstances.

6.2 CHLORIDE DETERMINATIONS IN WASTE

The proposed regulations will require analysis of total chloride in waste samples. It has been found that organochlorine is essentially completely converted to HCl and, when a source of hydrogen ions is present, inorganic chlorides are also converted to HCl. Thus, the measurement of only organic chloride is not enough. Acceptable methods include ASTM Methods D-808-81 or E442.

SECTION 7.0

METALS MEASUREMENTS

This section covers the measurement of toxic metals in stack gases and waste. The section addresses the sampling and analysis of the 10 metals of concern described in Section II.B of the Draft Preamble for Hazardous Waste Incinerator Regulations. The metals consist of the carcinogens arsenic, beryllium, cadmium, and chromium(VI) and the noncarcinogens antimony, barium, lead, mercury, silver, and thallium. The proposed metals train sampling procedure addresses metals found in the stack gases as particulates or volatile metal vapors. The methods of sampling and analysis for the 10 metals are summarized in Table 7.1.

7.1 SAMPLING AND ANALYSIS OF WASTE

The sampling and analysis of wastes are adequately addressed by specific sections in SW-846. These sections consist of Chapter 3 of Part I, which contains a discussion of sampling considerations and sample preparations, and Methods 3005, 3010, 3020, 3040, and 3050, which cover various methods of digesting the samples prior to analysis.

In Section 3.3 of SW 846 methods are provided for the analysis of all 10 of the metals of interest. The methods consist of Method 6010, inductively coupled plasma atomic emission spectroscopy (ICP), direct aspiration, and furnace atomic absorption. In addition, the gaseous hydride Method 7061 for arsenic and the manual cold-vapor techniques for mercury consisting of Method 7470, mercury in liquids, and Method 7471, mercury in solids, are also described. Four methods are provided for the analysis of hexavalent chromium. All of these methods should prove satisfactory for the analysis of solid and/or liquid wastes.

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TABLE 7.1 SAMPLING AND ANALYSIS METHODS

Sample	Sampling procedure	Constituent	Analysis method
Flue gas	EPA Method 5	Particulates	
	Multiple Metals Train	Total metals[a]	See methods listed below
		Antimony	7041
		Arsenic[b]	7060,[c] 7061[c]
		Barium	6010, 7080
		Beryllium[b]	6010, 7090, 7091
		Cadmium	6010, 7130, 7131
		Chromium (total)	6010, 7190, 7191
		Chromium(VI)	7195-7198[d]
		Lead[b]	6010, 7420, 7421
		Mercury[b]	7470,[c] 7471[e]
		Silver	6010, 7760[e]
		Thallium	6010, 7841
	Individual Metals Methods		
	EPA Method 108	Arsenic	7060,[c] 7061[b]
	EPA Methods 103, 104	Beryllium	6010, 7090, 7091
	EPA Method 12	Lead	6010, 7420, 7421
	EPA Method 101A	Mercury	7470,[c] 7471[e]

(continued)

TABLE 7.1 (continued)

Sample	Sampling procedure	Constituent	Analysis method
Other samples[f]	Composite	Antimony	7040
		Arsenic	7060,[c] 7061[c]
		Barium	6010, 7080
		Beryllium	6010, 7090, 7091
		Cadmium	6010, 7130, 7131
		Chromium (total)	6010, 7190, 7191
		Chromium(VI)	7195-7198[d]
		Lead	6010, 7420, 7421
		Mercury	7470,[c] 7471[e]
		Silver	6010, 7760[e]
		Thallium	6010, 7841

[a] See discussion in text for explanation of the Multiple Metals Train.

[b] Digestion and/or analysis procedures given in the individual metals methods listed below take precedence over general methods listed here.

[c] This method includes digestion for aqueous matrices (no separate digestion method is necessary).

[d] These chromium(VI) methods are for aqueous matrices only.

[e] This method includes digestion for all matrices (no separate digestion method is necessary).

[f] Includes waste feed, bottom ash, and scrubber liquor.

7.2 SAMPLING AND ANALYSIS OF STACK GASES

The sampling and analysis for metals in stack gases require the use of a suitable sampling train and the analysis of the collected sample. In those cases where specific metals can be identified as potential emissions, sampling will probably be best addressed by selecting a specific sampling and analytical approach. Specific methods which have been developed included EPA Method 12 for lead, Method 101A for mercury, Methods 103 and 104 for beryllium, and Method 108 for arsenic.

In most cases, however, sampling will be required for all 10 of the metals. For this, the draft metals protocol "Methodology for the Determination of Trace Metal Emissions in Exhaust Gases From Stationary Source Combustion Processes" (prepared by the EPA, EMSL, Source Branch) describes the only system that has been proposed to collect both the volatile and nonvolatile fraction of the stack gases. A copy of this draft protocol is in Appendix E.

Once the samples have been recovered from the train and digested, the analytical procedures using ICAP or AAS as specified in Figure 2 of the draft protocol should prove adequate.

7.3 SPECIFIC CONSIDERATIONS

This section covers specific considerations for sampling and analyzing chromium(VI) and a discussion of digestion of solid samples.

The toxicity concern associated with chromium is related primarily to the metal in the hexavalent oxidation state. Therefore, the determination of chromium by its oxidation state becomes important. The procedures outlined in SW-846 achieve this determination by separating the chromium(VI) from the total chromium either before or during the analytical step. Method 7195 separates the chromium(VI) by chelation with ammonium pyrrolidine dithiocarbamate (APDC), followed by extraction with methyl isobutyl ketone (MIBK). The concentration of chromium(VI) in the MIBK is then determined. Method 7196 analyzes chromium(VI) by the production of a colored product with diphenyl-carbazide, which is then measured spectrophotometrically. These procedures should prove satisfactory for the analysis of waste feed material.

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There are, however, several areas of concern related to determining hexavalent chromium. These problems are the stability of the sample, the recovery efficiencies when separating low level samples, and the recovery of the chromium sample from the sample train.

EPA is currently working on a suitable procedure to collect chromium(VI) stack samples. No acceptable procedure for the sampling and analysis of chromium(VI) is currently available. Problems with stability of the sample have been found even when using a Method 5 type sampling train with stabilizing solutions in the impingers and dedicated solely to chromium(VI) sampling. Further research is being conducted to develop procedures for measuring chromium(VI) emissions.

Total chromium may be determined using the multiple metals train.

The development of a suitable protocol to cover the digestion of solid waste and particulate catches is an area that, in general, needs further investigation. The draft metals protocol employs a hydrofluoric acid/nitric acid digestion in microwave bombs for the probe rinse and filter samples resulting from stack sampling. It also offers an option of either a hydrofluoric acid/nitric acid digestion in microwave bombs or a nitric acid/ hydrogen peroxide digestion on a hot plate for the impinger contents except the potassium permanganate impinger, which is analyzed for mercury only. An aliquot of the other (combined) impinger contents is also reserved for mercury analysis. This method is described for arsenic, cadmium, chromium, lead, and mercury.

The hydrofluoric acid/nitric acid digestion primarily employed in this method is considered to be a total digestion. Hydrofluoric acid digestions dissolve samples which tend to be difficult to digest thoroughly with other digestions, especially those which are high in silicates. The use of the sealed microwave bombs lessens the likelihood that volatile elements such as arsenic could be lost during the digestion process, assuming no venting of the samples takes place during heating. Unfortunately, using the microwave bombs can result in high levels of carbon and carbon particulates in the samples due to saturation of the solutions with carbon during digestion. The carbon can

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cause interferences or other problems during analysis. Carbon is usually lost from other, open container digestions (i.e., Method 3050) by conversion to carbon dioxide.

There are, however, no provisions in this method for the preparation of process samples or guidelines for samples which contain excessive amounts of ash. Another drawback of the use of hydrofluoric acid digestions is the effect of these digests upon analysis instruments due to the hydrofluoric acid content and its corrosive and destructive properties. The need for the expensive microwave digestion system and the appropriate equipment to perform the hydrofluoric acid digestions is another concern of this method.

EPA SW-846 Method 3050 is a nitric acid/hydrogen peroxide digestion for sludges. The method makes provisions for digestions for both inductively coupled plasma (ICP) and graphite furnace atomic absorption (GFAA) analyses. This method is used to digest samples for the following elements: thallium by ICP; and arsenic, beryllium, cadmium, chromium, lead, and thallium by GFAA.

This method is described only for solids such as soil, sediments, and sludges; however, there may be times when a liquid may require a more rigorous digestion than is afforded by the methods available for liquid digests (EPA SW-846 Methods 3005, 3010, and 3020). Application of this method to liquids presents a more complete digestion of the sample with the use of hydrogen peroxide. Modification of the method would be necessary as a mere 1- to 2-g sample of the water would not give the sensitivity of Methods 3005, 3010, or 3020. A 100-mL sample per 100-mL final volume would retain the sensitivity of those methods while giving the more rigorous digestion. This method may not be amenable to organically based samples, such as some waste stream feed samples. EPA SW-846 Method 3040 (described below) is recommended for oily or greasy samples.

The digestions presented in this method for ICP and GFAA analyses parallel each other for several steps. Near the end of the procedure, the digests for each analysis type are split, and the ICP digests have hydrochloric acid added to them while the GFAA digests do not. When a sample may require both ICP and GFAA and cannot be aliquoted, such as a stack sampling

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train, one digest must be chosen if this method is employed. Given that the digests with the hydrochloric acid added cannot be analyzed using the graphite furnace due to their hydrochloric acid content, the GFAA portion of the method should be chosen. The presence or lack of hydrochloric acid does not adversely affect the ICP analysis.

EPA SW-846 Method 3040 is a method used to prepare samples containing (primarily) waxes, greases, or oils for analysis by dissolving the samples in xylenes. It is pointed out that this method is not a digestion procedure, but merely a solvent dissolution procedure. Samples which may be high in particulate material are not effectively digested by this procedure since most particulate material is not dissolved. The particulate material could be anticipated to contain a high percentage of the metals in the sample, and the analysis, therefore, might not be a "total" metal determination. This method is used to prepare samples for analysis by ICP or atomic absorption (method not specified) for antimony, beryllium, cadmium, and chromium.

This method employs the method of standard additions (MSA) for all samples. The use of an internal standard in ICP analysis can preclude the use of MSA and reduces the number of samples needed to produce the same results. It does, however, eliminate the element chosen as the internal standard from the analysis of the samples and assumes a low content of the samples for the chosen element.

APPENDIX A

PERFORMANCE SPECIFICATIONS FOR CONTINUOUS EMISSION MONITORING OF CARBON MONOXIDE AND OXYGEN IN HAZARDOUS WASTE INCINERATORS, BOILERS, AND INDUSTRIAL FURNACES

APPENDIX A--PERFORMANCE SPECIFICATIONS FOR CONTINUOUS EMISSION MONITORING OF CARBON MONOXIDE AND OXYGEN IN HAZARDOUS WASTE INCINERATORS, BOILERS, AND INDUSTRIAL FURNACES

1.0 Applicability and Principle

1.1 Applicability.

This specification is to be used for evaluating the acceptability of carbon monoxide (CO) and oxygen (O_2) continuous emission monitoring systems (CEMS) installed on hazardous waste incinerators, boilers, and industrial furnaces.

This specification is intended to be used in evaluating the acceptability of the CEMS at the time of or soon after installation and at other times as specified in the regulations. This specification is not designed to evaluate the CEMS performance over an extended period of time nor does it identify specific routine calibration techniques and other auxiliary procedures to assess CEMS performance. The source owner or operator, however, is responsible to calibrate, maintain, and operate the CEMS.

1.2 Principle.

Installation and measurement location specifications, performance and equipment specifications, test procedures, and data reduction procedures are included in this specification. Relative accuracy (RA) tests, calibration error (Ec) tests, calibration drift (CD) tests, and response time (RT) tests are conducted to determine conformance of the CEMS with the specification.

2.0 Definitions

2.1 Continuous Emission Monitoring System (CEMS).

The CEMS is comprised of all the equipment used to generate data and includes the sample extraction and transport hardware, the analyzer(s), and the data recording/processing hardware (and software).

2.2 Continuous.

A continuous monitor is one in which the sample to be analyzed passes the measurement section of the analyzer without interruption and which evaluates the detector response to the sample at least once each 15 s and records the average of these observations each and every min.

The hourly rolling average is the arithmetic mean of sixty (60) most recent 1-min average values recorded by the continuous monitoring system.

2.3 Monitoring System Types.

There are three basic types of monitoring systems: extractive, cross-stack. and in situ. Carbon monoxide monitoring systems generally are extractive or cross-stack, while oxygen monitors are either extractive or in situ.

2.3.1 Extractive.

Extractive systems use a pump or other mechanical, pneumatic, or hydraulic means to draw-a small portion of the stack or flue gas and convey it to the remotely located analyzer.

2.3.2 In situ.

In situ analyzers place the sensing or detecting element directly in the flue gas stream and thus perform the analysis without removing a sample from the stack.

2.3.3 Cross-stack.

Cross-stack analyzers measure the parameter of interest by placing a source beam on one side of the stack and either the detector (in single-pass instruments) or a retro-reflector (in double-pass instruments) on the other side and measuring the parameter of interest (e.g., CO) by the attenuation of the beam by the gas in its path.

2.4 Span.

The upper limit of the gas concentration measurement range specified Section 4.1.

2.5 Instrument Range.

The maximum and minimum concentration that can be measured by a specific instrument. The minimum is often stated or assumed to be zero (0) and the range expressed only as the maximum. If a single analyzer is used for measuring multiple ranges (either manually or automatically), the performance standards expressed as a percentage of full scale apply to all ranges.

2.6 Calibration Drift.

Calibration drift is the change in response or output of an instrument from a reference value over time. Drift is measured by comparing the responses to a reference standard over time with no adjustment of instrument settings.

2.7 Response Time.

The response time of a system or part of a system is the amount of time between a step change in the system input (e.g., change of calibration gas) until the data recorder displays 95 percent of the final value.

2.8 Accuracy.

Accuracy is a measure of agreement between a measured value and an accepted or true value and is usually expressed as the percentage difference between the true and measured values relative to the true value. For this performance specification the accuracy is checked by conducting a calibration error (Ec) test and a relative accuracy (RA) test.

2.8.1   Calibration Error.

Calibration error is a measure of the deviation of a measured value at the analyzer mid range from a reference value.

2.8.2   Relative Accuracy.

Relative accuracy is the comparison of the CEMS response to a value measured by a reference test method (RM). The applicable reference test methods are Method 10A--Determination of Carbon Monoxide in Certifying Continuous Emission Monitoring Systems at Petroleum Refineries and Method 3--Gas Analysis for Carbon Monoxide, Oxygen, Excess Air, and Dry Molecular Weight; these methods are found in 40 CFR 60, Appendix A.

3.0 Installation and Measurement Location Specifications

3.1 CEMS Measurement Location.

The best or optimum location of the sample interface for the monitoring system is determined by a number of factors, including ease of access for calibration and maintenance, the degree to which sample conditioning will be required, the degree to which it represents total emissions, and the degree to which it represents the combustion situation in the firebox. The location should be as free from in-leakage influences as possible and reasonably free from severe flow disturbances. The sample location should be at least two equivalent duct diameters downstream from the nearest control device, point of pollutant generation, or other point at which a change in the pollutant concentration or

emission rate occurs and at least 0.5 diameters upstream from the exhaust or control device. The equivalent duct diameter is calculated as per 40 CFR 60, Appendix A, Method 1, Section 2.1.

The sample path or sample point(s) should include the concentric inner 50 percent of the stack or duct cross section. For circular ducts, this is 0.707 x diameter and a single-point probe, therefore, should be located between 0.141 x diameter and 0.839 x diameter from the stack wall and a multiple-point probe should have sample inlets in this region. A location which meets both the diameter and the cross-section criteria will be acceptable.

If these criteria are not achievable or if the location is otherwise less than optimum, the possibility of stratification should be investigated. To check for stratification, the oxygen concentration should also be measured as verification of oxygen in-leakage. For rectangular ducts, at least nine sample points located at the center of similarly shaped, equal area divisions of the cross section should be used. For circular ducts, 12 sample points (i.e., six points on each of the two perpendicular diameters) should be used, locating the points as described in 40 CFR 60, Appendix A, Method 1. Calculate the mean value for all sample points and select the point(s) or path that provides a value equivalent to the mean. For these purposes, if no single value is more than 15 percent different from the mean and if no two single values are different from each other by more than 20 percent of the mean, then the gas can be assumed homogeneous and can be sampled anywhere. The point(s) or path should be within the inner 50 percent of the area.

Both the oxygen and CO monitors should be installed at the same location or very close to each other. If this is not possible, they may be installed at different locations if the effluent gases at both sample locations are not stratified and there is no in-leakage of air between sampling locations.

3.2 Reference Method (RM) Measurement Location and Traverse Points.

Select, as appropriate, an accessible RM measurement point at least two equivalent diameters downstream from the nearest control device, the point of

pollutant generation, or other point at which a change in the pollutant concentration or emission rate may occur, and at least a half equivalent diameter upstream from the effluent exhaust or control device. When pollutant concentration changes are due solely to oxygen in-leakage (e.g., air heater leakages) and pollutants and diluents are simultaneously measured at the same location, a half diameter may be used in lieu of two equivalent diameters. The CEMS and RM locations need not be the same. Then select traverse points that assure acquisition of representative samples over the stack or duct cross section. The minimum requirements are as follows: Establish a "measurement line" that passes through the centroidal area and in the direction of any expected stratification. If this line interferes with the CEM measurements, displace the line up to 30 cm (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area. Locate three traverse points at 16.7, 50.0, and 83.3 percent of the measurement line. If the measurement line is longer than 2.4 m and pollutant stratification is not expected, the tester may choose to locate the three traverse points on the line at 0.4, 1.2, and 2.0 m from the stack or duct wall. This option must not be used at points where two streams with different pollutant concentrations are combined. The tester may select other traverse points, provided that they can be shown to the satisfaction of the Administrator to provide a representative sample over the stack or duct cross section. Conduct all necessary RM tests within 3 cm (but no less than 3 cm from the stack or duct wall) of the traverse points.

4.0 Monitoring System Performance Specifications

Table A-1 summarizes the performance standards for the continuous monitoring systems. Each of the items is discussed in the following paragraphs. Two sets of standards for CO are given--one for low range measurement and another for high range measurement since the proposed CO limits are dual range. The high range standards relate to measurement and quantification of short duration high concentration-peaks, while the low range standards relate to the overall average operating condition of the incinerator. The dual-range specification can be met either by using two separate analyzers, one for each

range, or by using dual range units which have the capability of meeting both standards with a single unit. In the latter case, when the reading goes above the full scale measurement value of the lower range, the higher range operation will be started automatically.

TABLE A-1.   PERFORMANCE SPECIFICATIONS OF CO AND OXYGEN MONITORS

Parameter	CO monitors		Oxygen monitors
	Low range	High range	
Calibration drift 24 h	$\leq$ 5% FS[a]	$\leq$ 5% FS	$\leq$ 0.5% O_2
Calibration error[b]	$\leq$ 5% FS	$\leq$ 5% FS	$\leq$ 0.5% O_2
Response time	$\leq$ 1.5 min	$\leq$ 1.5 min	$\leq$ 15 min
Relative accuracy	$\leq$ The greater of 10% of RM or 20 ppm		$\leq$ The greater of 20% of RM or 1.0% O_2

[a] FS means full scale measurement range.

[b] Expressed as the sum of the mean absolute value plus the 95% confidence interval of a series of measurements.

4.1 CEMS Span Values.

The span values shown below in Table A-2 are to be established for the continuous emission monitoring system.

TABLE A-2. CEMS SPAN VALUES FOR CO AND OXYGEN MONITORS

| | CO monitors | | Oxygen monitors (%) |
	Low range (ppm)	High range (ppm)	
Tier 1 rolling average format	200	3,000	25
Tier 1 alternate format	200	3,000	25
Tier 2 rolling average format	2 x permit limit	3,000	25
Tier 2 alternate format	2 x permit limit	1.1 x permitted peak value	25

4.2 System Measurement Range.

In order to measure both the high and low concentrations consistently with the same or similar degree of accuracy, system measurement range maximum span specifications are given for both the low and high range monitors. The system measurement range chosen is based upon the permitted level and the span value presented in Section 4.1.

The owner or operator must choose a measurement range that includes zero and a high-level value. The high-level value is chosen by the source owner and operator as follows:

1. For the low range CO measurements, the high level value is set between 1.5 times the permit limit and the span value specified in Section 4.1.

2. For the high range CO measurement, except for Tier II alternate format, the high level value is set between 2000 ppm, as a minimum, and the span value specified in Section 4.1.

3. For the high range CO measurement under Tier II using the alternate type B format, the high level value is set at the span value specified in Section 4.1.

4. For oxygen the high level value is set between 1.5 times the highest level measured during the trial burn and the span value specified in Section 4.1.

The calibration gas, or gas cell values used to establish the data recorder scale should produce the zero and high level values.

4.3 Response Time.

The mean response time for the CO monitor(s) should not exceed 1.5 min to achieve 95 percent of the final stable value. For the oxygen monitor, the mean response time should not exceed 15 min to achieve 95 percent of the final stable value.

4.4 Calibration Drift.

The CEMS calibration must not drift or deviate from the reference value of the gas cylinder or gas cell by more than 5 percent full scale in 24 h for the CO low range and the CO high range. For oxygen the calibration drift must be less than 0.5 percent O_2 in 24 h. The calibration drift specification must not be exceeded for six out of the seven test days required during the test (see Section 5 for the test procedures).

4.5 Calibration Error.

The calibration error specification evaluates the system accuracy at the midpoint of the measurement range by the calibration error test described in Section 6. The test determines the difference between the measured value and the expected value at this midpoint.

The calibration error of the CEMS must not exceed 5 percent full scale for CO. The calibration error of the oxygen CEMS must not exceed 0.5 percent O_2.

4.6 Relative Accuracy.

The relative accuracy (RA) of the carbon monoxide CEMS must not exceed 10 percent of the mean value of the reference method (RM) test data or 20 ppm CO, whichever is greater. Note that during the relative accuracy test, the CO level may exceed the full scale of the low range monitor. When this occurs, the mean CEMS measurement value should be calculated using the appropriate data from both the low range and high range monitors.

The relative accuracy of the oxygen CEMS must not exceed 20 percent of the mean value of the RM test data or 1 percent oxygen, whichever is greater.

5.0 Performance Specification Test Period

5.1 Pretest Preparation.

Install the CEMS, prepare the RM test site according to the specifications in Section 3, and prepare the CEMS for operation according to the manufacturer's written instructions.

5.2 Calibration Error and Response Time Tests.

Prior to initiating the calibration drift tests conduct the calibration error test and the response time test according to the test procedures established in Section 6. The carbon monoxide and oxygen (if applicable) monitoring systems must be evaluated separately.

5.3 Calibration Drift Test Period.

The monitoring system should be operated for some time before attempting drift checks because most systems need a period of equilibration and adjustment

before the performance is reasonably stable. At least one week (168 h) of continuous operation is recommended before attempting drift tests.

While the facility is operating at normal conditions, determine the magnitude of the calibration drift (CD) once each day (at 24-h intervals) for seven consecutive days according to the procedure given in Section 6. The carbon monoxide and oxygen (if applicable) monitoring systems must be evaluated separately.

5.4 RA Test Period.

Conduct the RA test according to the procedure given in Section 6 while the facility is operating at normal conditions. The RA test may be conducted during the CD test period. The RA test may be conducted separately for each of the monitors (carbon monoxide and oxygen, if applicable) or may be conducted as a combined test so that the results are calculated only for the corrected CO concentration (i.e., CO corrected to 7 percent oxygen); the latter approach is preferred.

6.0 Performance Specification Test Procedures

6.1 Response Time.

The response time tests apply to all types of monitors, but will generally have significance only for extractive systems. The entire system is checked with this procedure including sample extraction and transport (if applicable), sample conditioning (if applicable), gas analyses, and the data recording.

Introduce zero gas into the system. For extractive systems, the calibration gases should be introduced at the probe as near to the sample location as possible. For in situ systems, introduce the zero gas at the sample interface so that all components active in the analysis are tested. When the system output has stabilized (no change greater than 1 percent of full scale for 30 s), switch to monitor stack effluent and wait for a stable value. Record the time

(upscale response time) required to reach 95 percent of the final stable value. Next, introduce a high level calibration gas and repeat the above procedure (stable, switch to sample, stable, record). Repeat the entire procedure three times and determine the mean upscale and downscale response times. The slower or longer of the two means is the system response time.

6.2 Calibration Error Test

6.2.1 Procedure.

The procedure for testing calibration error is to set the instrument zero and span with the appropriate standards and then repeatedly measure a standard in the middle of the range. In order to minimize bias from previous analyses, the sequence of standard introduction should alternate between high and low standards prior to the mid-level standard (e.g., high, mid, low, mid, high, mid, low, mid, etc.) until six analyses of the mid-level standard are obtained, with three values obtained from upscale approach and three values obtained from downscale approach.

The differences between the measured instrument output and the expected output of the reference standards are used as the data points.

6.2.2 Calculations.

Summarize the results on a data sheet. For each of the six measurements made, calculate the arithmetic difference between the midpoint reference value and the measured value. Then calculate the mean of the difference, standard deviation, confidence coefficient, and calibration error using Equations 2-1, 2-2, 2-3, and 2-4 presented in Section 7.

6.3 Zero and Span Calibration Drift.

The purpose of the calibration drift (CD) checks is to determine the ability of the CEMS to maintain its calibration over a specified period of time. The performance specifications establish a standard related to span drift. Each

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drift test is conducted seven times and the system(s) are allowed to exceed the limit once during the test.

During the drift tests, no adjustment of the system is permitted except those automatic internal adjustments which are part of the automatic compensation circuits integral to the analyzer. If periodic automatic adjustments are made to the CEMS zero and calibration settings, conduct the daily CD test immediately before these adjustments, or conduct it in such a way that the CD can be determined (calculated). Subsequent CEMs operation must include the same system configuration as used during the performance testing.

Select a reference gas with a CO or O_2 concentration between 80 and 100 percent of the full-scale measurement range of the analyzer; ambient air (20.9 percent O_2) may be used as the reference gas for oxygen. The zero gas should contain the lowest concentration recommended by the manufacturer. Prior to the test, calibrate the instrument. At the beginning of the test, introduce the selected zero and span reference gases (or cells or filters). After 24 h and at 24-h intervals thereafter, alternately introduce both the zero and span reference gases, wait until a stable reading is obtained and record the values reported by the system. Subtract the recorded CEMS response from the reference value. Repeat this procedure for 7 days, obtaining eight values of zero and span gas measurements (the initial values and seven 24-h readings). The difference between the established or reference value for the span and the measured value may not exceed the specifications in Table 4.1 more than once, and the average value must not exceed the specification.

6.4 Relative Accuracy Test Procedure

6.4.1 Sampling Strategy for RM Tests.

Conduct the RM tests in such a way that they will yield results representative of the emissions from the source and can be correlated to the CEMS data. Although it is preferable to conduct the oxygen, moisture (if needed), and CO measurements simultaneously, the diluent and moisture measurements that are taken within a 30- to 60-min period which includes the pollutant measurements,

may be used to calculate dry pollutant concentration corrected to 7 percent O_2.

In order to correlate the CEMS and RM data properly, mark the beginning and end of each RM test period of each run (including the exact time of the day) on the CEMS chart recordings or other permanent record of output. The RM tests should utilize integrated sampling.

For each run, make a sample traverse of at least 21 min, sampling for 7 min per point.

6.4.2   Correlation of RM and CEMS Data.

Correlate the CEMS and the RM test data as to the time and duration by first determining from the CEMS final output (the one used for reporting) the integrated average pollutant concentration during each pollutant RM test period. Consider system response time, if important, and confirm that the pair of results are on a consistent moisture, temperature, and diluent concentration basis. Then, compare each integrated CEMS value against the corresponding average RM value. Make a direct comparison of the RM results and CEMS integrated average value. When oxygen monitoring is required by the regulation to calculate carbon monoxide normalized to 7 percent O_2, the RM test results should be calculated and compared on this basis. That is, the CO concentrations normalized to 7 percent O_2 should be calculated using the RM test data and these results should be compared to the CO concentration normalized to 7 percent O_2 measured by the CEMS.

6.4.3   Number of RM Tests.

Conduct a minimum of nine sets of all necessary RM tests.

Note: The tester may choose to perform more than nine sets of RM tests. If this option is chosen, the tester may, at their discretion, reject a maximum of three sets of the test results so long as the total number of test results

used to determine the RA is greater than or equal to nine, but they must report all data including the rejected data.

6.4.4   Calculations.

Summarize the results on a data sheet. Calculate the mean of the RM values. Calculate the arithmetic differences between the RM and the CEMS output sets. Then calculate the mean of the difference, standard deviation, confidence coefficient, and CEMS RA, using Equations 2-1, 2-2, 2-3, and 2-5.

7.0 Equations

7.1 Arithmetic Mean.

Calculate the arithmetic mean of the difference, d, of a data set as follows:

$$\bar{d} = \frac{1}{n} \sum_{i=1}^{n} d_i \qquad\qquad \text{(Eq. 2-1)}$$

Where n = number of data points

$$\sum_{i=1}^{n} d_i = \text{algebraic sum of the individual differences } d_i$$

When the mean of the differences of pairs of data is calculated, be sure to correct the data for moisture, if applicable.

7.2 Standard Deviation.

Calculate the standard deviation, S_d, as follows:

$$S_d = \left[\frac{\sum_{i=1}^{n} d_i^2 - \left(\frac{\sum_{i=1}^{n} d_i}{n} \right)^2}{n - 1} \right]^{1/2} \qquad\qquad \text{(Eq. 2-2)}$$

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7.3 Confidence Coefficient.

Calculate the 2.5 percent error confidence coefficient (one-tailed), CC, as follows:

$$CC = t_{0.975} \frac{S_d}{(n)^{1/2}} \qquad \text{(Eq. 2-3)}$$

Where $t_{0.975}$ = t-value (see Table 7-1).

TABLE 7-1. VALUES

n^a	$t_{0.975}$	n^a	$t_{0.975}$	n^a	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.262	15	2.145
6	2.571	11	2.228	16	2.131

[a] The values in this table are already corrected for n-1 degrees of freedom. Use n equal to the number of individual values.

7.4 Calibration Error.

Calculate the calibration error (Ec) of a set of data as follows:

For carbon monoxide:

$$E_c = \frac{|\bar{d}| + |CC|}{FS} \times 100 \qquad \text{(Eq. 2-4)}$$

For oxygen:* $E_c = |\bar{d}| + |CC|$

where: $|d|$ = absolute value of the mean of differences (from Equation 2-1)

$|CC|$ = absolute value of the confidence coefficient (from Equation 2-3)

FS = full scale span of monitoring system (for calculation of CO calibration error only)

7.5 Relative Accuracy.

Calculate the relative accuracy (RA) of a set of data as follows:

$$RA = \frac{|\bar{d}| + |CC|}{RM} \times 100 \qquad (Eq.\ 2\text{-}5)$$

where $|d|$ = absolute value of the mean of differences (from Equation 2-1)

$|CC|$ = absolute value of the confidence coefficient (from Equation 2-3)

RM = average RM value

8.0 Reporting

At a minimum (check with the appropriate regional office, or state, or local agency for additional requirements, if any) summarize in tabular form the results of the response time tests, calibration error tests, calibration drift tests, and the relative accuracy tests. Include all data sheets, calculations, charts (records of CEMS responses), cylinder gas concentration certifications, and calibration cell response certifications (if applicable), necessary to substantiate that the performance of the CEMS met the performance specifications.

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* For oxygen the calibration error is expressed as % O_2 and the term $[|d| + |CC|]$ is not divided by FS or multiplied by 100.

9.0 References

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APPENDIX B

METHODS FOR MOISTURE AND OXYGEN MEASUREMENTS:
EPA METHODS 3, 4, AND 5

plicable for some or all of the above determinations. Examples of specific methods and modifications include: (1) a multi-point sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point (2) a method using CO_2 or O_2 and stoichiometric calculations to determine dry molecular weight and excess air (3) assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil. These methods and modifications may be used, but are subject to the approval of the Administrator, U.S. Environmental Protection Agency.

2. Apparatus

As an alternative to the sampling apparatus and systems described herein, other sampling systems (e.g., liquid displacement) may be used provided such systems are capable of obtaining a representative sample and maintaining a constant sampling rate, and are otherwise capable of yielding acceptable results. Use of such systems is subject to the approval of the Administrator.

2.1 Grab Sampling (Figure 3-1).

2.1.1 Probe. The probe should be made of stainless steel or borosilicate glass tubing and should be equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Any other materials inert to O_2, CO_2, CO, and N, and resistant to temperature at sampling conditions may be used for the probe; examples of such material are aluminum, copper, quartz glass and Teflon.

2.1.2 Pump. A one-way squeeze bulb, or equivalent, is used to transport the gas sample to the analyzer.

2.2 Integrated Sampling (Figure 3-2).

2.2.1 Probe. A probe such as that described in Section 2.1.1 is suitable.

Method 3—Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight

1. Principle and Applicability

1.1 Principle. A gas sample is extracted from a stack, by one of the following methods: (1) single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent carbon dioxide (CO_2), percent oxygen (O_2), and, if necessary, percent carbon monoxide (CO). If a dry molecular weight determination is to be made, either an Orsat or a Fyrite[*] analyzer may be used for the analysis; for excess air or emission rate correction factor determination, an Orsat analyzer must be used.

1.2 Applicability. This method is applicable for determining CO_2 and O_2 concentrations, excess air, and dry molecular weight of a sample from a gas stream of a fossil-fuel combustion process. The method may also be applicable to other processes where it has been determined that compounds other than CO_2, O_2, CO, and nitrogen (n,) are not present in concentrations sufficient to affect the results.

Other methods, as well as modifications to the procedure described herein, are also ap-

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[*] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.
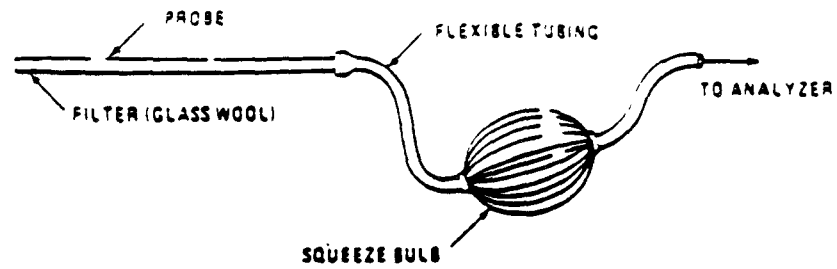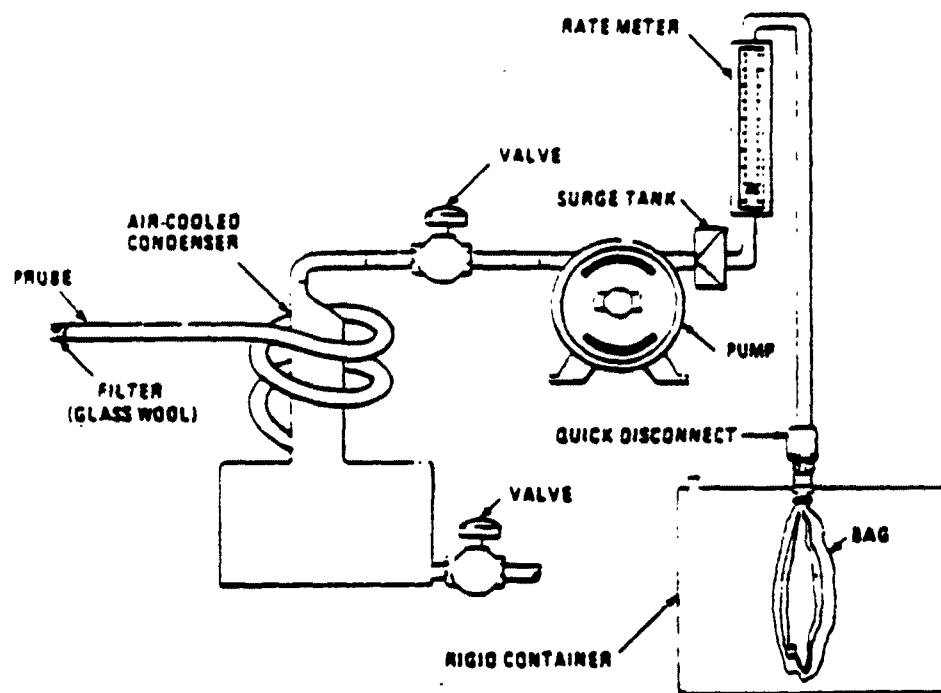
Figure 3-1 Grab sampling train

Figure 3-2. Integrated gas-sampling train.

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2.2.2 Condenser. An air cooled or water-cooled condenser, or other condenser that will not remove O_2, CO_2, CO. and N_2, may be used to remove excess moisture which would interfere with the operation of the pump and flow meter.

2.2.3 Valve. A needle valve is used to adjust sample gas flow rate.

2.2.4 Pump. A leak-free, diaphragm-type pump. or equivalent. is used to transport sample gas to the flexible bag. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.2.5 Rate Meter. The rotameter, or equivalent rate meter. used should be capable of measuring flow rate to within ±2 percent of the selected flow rate. A flow rate range of 500 to 1000 cm³/min is suggested.

2.2.6 Flexible Bag. Any leak-free plastic (e.g., Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g., aluminized Mylar) bag, or equivalent, having a capacity consistent with the selected flow rate and time length of the test run, may be used. A capacity in the range of 55 to 90 liters is suggested.

To leak-check the bag, connect it to a water manometer and pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. An alternative leak-check method is to pressurize the bag to 5 to 10 cm H_2O (2 to 4 in. H_2O) and allow to stand overnight. A deflated bag indicates a leak.

2.2.7 Pressure Gauge. A water-filled U-tube manometer, or equivalent, of about 28 cm (12 in.) is used for the flexible bag leak-check.

2.2.8 Vacuum Gauge. A mercury manometer, or equivalent, of at least 760 mm Hg (30 in. Hg) is used for the sampling train leak-check.

2.3 Analysis. For Orsat and Fyrite analyzer maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless otherwise specified herein.

2.3.1 Dry Molecular Weight Determination. An Orsat analyzer or Fyrite type combustion gas analyzer may be used.

2.3.2 Emission Rate Correction Factor or Excess Air Determination. An Orsat analyzer must be used. For low CO₂ (less than 4.0 percent) or high O₂ (greater than 15.0 percent) concentrations, the measuring burette of the Orsat must have at least 0.1 percent subdivisions.

3. Dry Molecular Weight Determination

Any of the three sampling and analytical procedures described below may be used for determining the dry molecular weight.

3.1 Single-Point, Grab Sampling and Analytical Procedure.

3.1.1 The sampling point in the duct shall either be at the centroid of the cross section or at a point no closer to the walls than 1.00 m (3.3 ft) unless otherwise specified by the Administrator.

3.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. If and Orsat analyzer is used, it is recommended that the analyzer be leaked-checked by following the procedure in Section 5; however, the leak-check is optional.

3.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point, purge the sampling line. Draw a sample into the analyzer and immediately analyze it for percent CO₂ and percent O₂. Determine the percentage of the gas that is N₂ and CO by subtracting the sum of the percent CO₂ and percent O₂ from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.1.4 Repeat the sampling, analysis, and calculation procedures, until the dry molecular weights of any three grab samples differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (lb/lb-mole).

3.2 Single-Point, Integrated Sampling and Analytical Procedure.

3.2.1 The sampling point in the duct shall be located as specified in Section 3.1.1.

3.2.2 Leak-check (optional) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (optional) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag and make sure that all connections are tight and leak free.

3.2.3 Sample at a constant rate. The sampling run should be simultaneous with, and for the same total length of time as the pollutant emission rate determination. Collection of at least 30 liters (1.00 ft³) of sample gas is recommended; however, smaller volumes may be collected, if desired.

3.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. Within 8 hours after the sample is taken, analyze it for percent CO₂ and percent O₂, using either an Orsat analyzer or a Fyrite-type combustion gas analyzer. If an Orsat analyzer is used, it is recommended that the Orsat leak-check described in Section 5 be performed before this determination; however, the check is optional.

Determine the percentage of the gas that is N_1 and CO by subtracting the sum of the percent CO_1 and percent O_1 from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.2.5 Repeat the analysis and calculation procedures until the individual dry molecular weights for any three analyses differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

3.3 Multi-Point, Integrated Sampling and Analytical Procedure.

3.3.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used for all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to approval of the Administrator.

3.3.2 Follow the procedures outlined in sections 3.2.2 throught 3.2.5, except for the following: traverse all sampling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-3.

4. *Emission Rate Correction Factor or Excess Air Determination*

NOTE: A Fyrite-type combustion gas analyzer is not acceptable for excess air or emission rate correction factor determination, unless approved by the Administrator. If both percent CO_1 and percent O_1 are measured, the analytical results of any of the three procedures given below may also be used for calculating the dry molecular weight.

Each of the three procedures below shall be used only when specified in an applicable subpart of the standards. The use of these procedures for other purposes must have specific prior approval of the Administrator.

4.1 Single-Point, Grab Sampling and Analytical Procedure.

4.1.1 The sampling point in the duct shall either be at the centroid of the cross-section or at a point no closer to the walls than 1.00 m (3.3 ft), unless otherwise specified by the Administrator.

4.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. Leak-check the Orsat analyzer according to the procedure described in Section 5. This leak-check is mandatory.

FIGURE 3-3—SAMPLING RATE DATA

Time	Traverse pt	Q-gm	% dev*
Average.			

*% Dev = $(C - C_{avg})/C_{avg} \times 100$ (Must be <10%)

4.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Draw a sample into the analyzer. For emission rate correction factor determination, immediately analyze the sample, as outlined in Sections 4.1.4 and 4.1.5, for percent CO_1 or percent O_1. If excess air is desired, proceed as follows: (1) immediately analyze the sample, as in Sections 4.1.4 and 4.1.5, for percent CO_1, O_1, and CO; (2) determine the percentage of the gas that is N_1 by subtracting the sum of the percent CO_1, percent O_1, and percent CO from 100 percent; and (3) calculate percent excess air as outlined in Section 6.2.

4.1.4 To insure complete absorption of the CO_1, O_1, or if applicable, CO, make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three or four) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.)

4.1.5 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis.

NOTE: Since this single-point, grab sampling and analytical procedure in normally conducted in conjunction with a single-point, grab sampling and analytical procedure for a pollutant, only one analysis is ordinarily conducted. Therefore, great care must be taken to obtain a valid sample and analysis. Although in most cases only CO_1 or O_1 is required, it is recommended that both CO_1 and O_1 be measured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4.2 Single-Point, Integrated Sampling and Analytical Procedure.

4.2.1 The sampling point in the duct shall be located as specified in Section 4.1.1.

4.2.2 Leak-check (mandatory) the flexible bag as in Section 2.1.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (mandatory) the train by placing a vacuum gauge at the condenser

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met pulling a vacuum of at least 250 mm Hg (10 in. Hg) plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum shall remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag and make sure that all connections are tight and leak free.

4.2.3 Sample at a constant rate, or as specified by the Administrator. The sampling run must be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collect at least 30 liters (1.00 ft³) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

4.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO_2 or percent O_2 (as outlined in Sections 4.2.5 through 4.2.7). The Orsat analyzer must be leak-check (see Section 5) before the analysis. If excess air is desired, proceed as follows: (1) within 4 hours after the sample is taken, analyze it (as in Sections 4.2.5 through 4.2.7) for percent CO_2, O_2, and CO; (2) determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2, percent O_2, and percent CO from 100 percent; (3) calculate percent excess air, as outlined in Section 6.2.

4.2.5 To insure complete absorption of the CO_2, O_2, or if applicable, CO, make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three or four) should be make between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.)

4.2.6 Repeat the analysis until the following criteria are met:

4.2.6.1 For percent CO_2, repeat the analytical procedure until the results of any three analyses differ by no more that (a) 0.3 percent by volume when CO_2 is greater than 4.0 percent or (b) 0.2 percent by volume when CO_2 is less than or equal to 4.0 percent. Average the three acceptable values of percent CO_2 and report the results to the nearest 0.1 percent.

4.2.6.2 For percent O_2, repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when O_2 is less than 15.0 percent or (b) 0.2 percent by volume when O_2 is greater than or equal to 15.0 percent. Average the three acceptable values of percent O_2 and report the results to the nearest 0.1 percent.

4.2.6.3 For percent CO, repeat the analytical procedure until the results of any three analyses differ by no more than 0.3

percent. Average the three acceptable values of percent CO and report the results to the nearest 0.1 percent.

4.2.7 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before an after the analysis.

NOTE: Although in most instances only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4.3 Multi-Point, Integrated Sampling and Analytical Procedure.

4.3.1 Both the minimum number of sampling points and the sampling point location shall be as specified in Section 3.1.1 of this method. The use of fewer points than specified is subject to the approval of the Administrator.

4.3.2 Follow the procedures outlined in Sections 4.2.2 through 4.2.7, except for the following: Traverse all sampling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-3.

5. *Leak-Check Procedure for Orsat Analyzers*

Moving an Orsat analyzer frequently causes it to leak. Therefore, an Orsat analyzer should be throughly leak-checked on site before the flue gas sample is introduced into it. The procedure for leak-checking an Orsat analyzer is:

5.1.1 Bring the liquid level in each pipette up to the reference mark on the capillary tubing and then close the pipette stopcock.

5.1.2 Raise the leveling bulb sufficiently to bring the confining liquid meniscus onto the graduated portion of the burette and then close the manifold stopcock.

5.1.3 Record the meniscus position.

5.1.4 Observe the meniscus in the burette and the liquid level in the pipette for movement over the next 4 minutes.

5.1.5 For the Orsat analyzer to pass the leak-check, two conditions must be met.

5.1.5.1 The liquid level in each pipette must not fall below the bottom of the capillary tubing during this 4-minute interval.

5.1.5.2 The meniscus in the burette must not change by more than 0.2 ml during this 4-minute interval.

5.1.6 If the analyzer fails the leak-check procedure, all rubber connections and stopcocks should be checked until the cause of the leak is identified. Leaking stopcocks must be disassembled, cleaned, and regreased. Leaking rubber connections must be replaced. After the analyzer is reassembled, the leak-check procedure must be repeated.

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6. Calculations

6.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).

%EA = Percent excess air.

%CO, = Percent CO, by volume (dry basis).

%O, = Percent O, by volume (dry basis).

%CO = Percent CO by volume (dry basis).

%N, = Percent N, by volume (dry basis).

0.264 = Ratio of O, to N, in air, v/v.

0.280 = Molecular weight of N, or CO, divided by 100.

0.320 = Molecular weight of O, divided by 100.

0.440 = Molecular weight of CO, divided by 100.

6.2 Percent Excess Air. Calculate the percent excess air (if applicable), by substituting the appropriate values of percent O,, CO, and N, (obtained from Section 4.1.3 or 4.2.4) into Equation 3-1.

% EA =

$$\frac{\%O_2 - 0.5\% CO}{0.264\% N_2 (\%O_2 - 0.5\% CO)} \times 100$$

Equation 3-1

NOTE: The equation above assumes that ambient air is used as the source of O, and that the fuel does not contain appreciable amounts of N, (as do coke oven or blast furnace gases). For those cases when appreciable amounts of N, are present (coal, oil, and natural gas do not contain appreciable amounts of N,) or when oxygen enrichment is used, alternate methods, subject to approval of the Administrator, are required.

6.3 Dry Molecular Weight. Use Equation 3-2 to calculate the dry molecular weight of the stack gas

$M_d = 0.440(\%CO_2) - 0.320(\%O_2) +$

$0.280(\%N_2 - \%CO)$

Equation 3-2

NOTE: The above equation does not consider argon in air (about 0.9 percent, molecular weight of 37.7). A negative error of about 0.4 percent is introduced. The tester may opt to include argon in the analysis using procedures subject to approval of the Administrator.

7. Bibliography

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METHOD 4—DETERMINATION OF MOISTURE CONTENT IN STACK GASES

1. Principle and Applicability

1.1 Principle. A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

1.2 Applicability. This method is applicable for determining the moisture content of stack gas.

Two procedures are given. The first is a reference method, for accurate determinations of moisture content (such as are needed to calculate emission data). The second is an approximation method, which provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content, e.g., drying tubes, wet bulb-dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc., are also acceptable.

The reference method is often conducted simultaneously with a pollutant emission measurement run; when it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent; these calculations shall not be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, U.S. Environmental Protection Agency, to be capable of yielding results within 1 percent H_2O of the reference method.

NOTE: The reference method may yield questionable results when applied to saturated gas streams or to streams that contain water droplets. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor (capable of measuring to ±1° C (2° F)) to the reference method probe. Measure

the stack gas temperature at each traverse point (see Section 2.2.1) during the reference method traverse; calculate the average stack gas temperature. Next, determine the moisture percentage, either by (1) using a psychrometric chart and making appropriate corrections if stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the pyschrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alter-

nate methods, subject to the approval of the Administrator shall be used.

2. *Reference Method*

The procedure described in Method 5 for determining moisture content is acceptable as a reference method.

2.1 Apparatus. A schematic of the sampling train used in this reference method is shown in Figure 4-1. All components shall be maintained and calibrated according to the procedure outlined in Method 5.
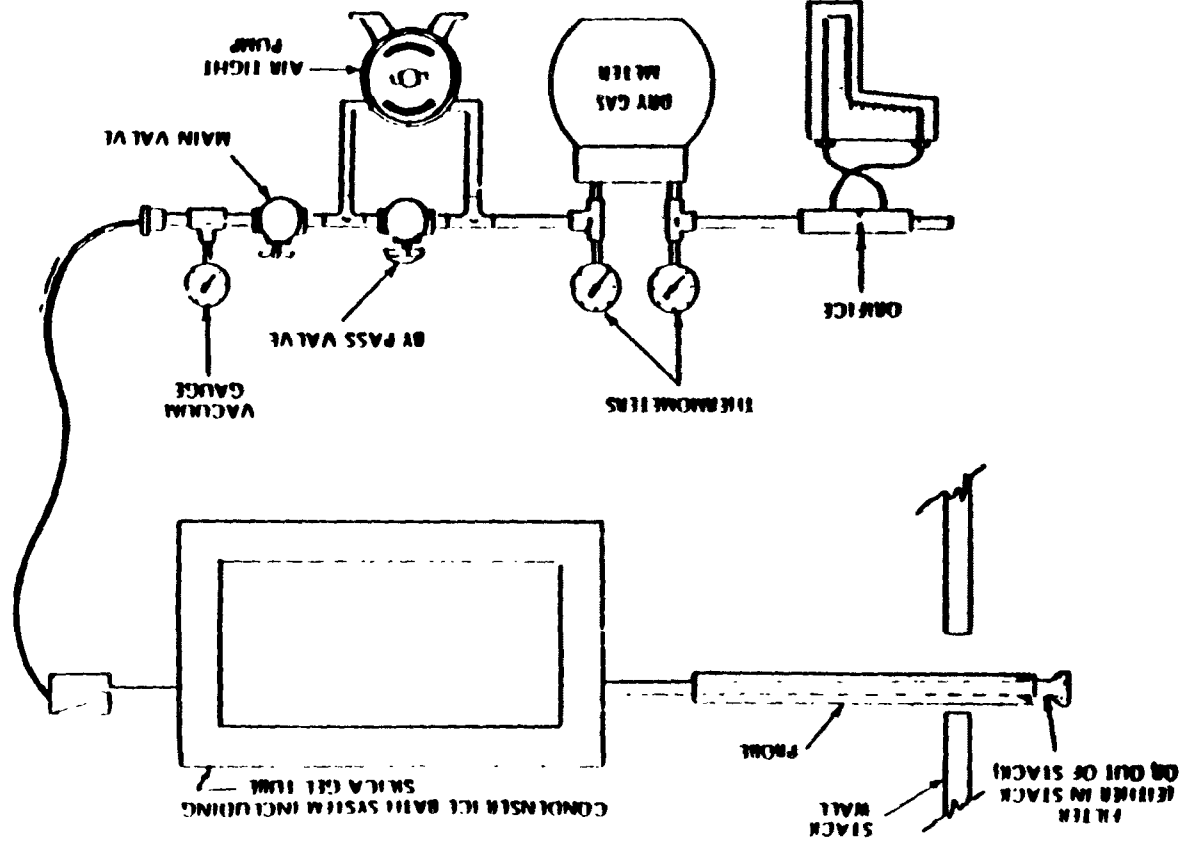
Figure 4-1 Moisture sampling train reference method

2.1.1 Probe. The probe is constructed of stainless steel or glass tubing, sufficiently heated to prevent water condensation, and is equipped with a filter, either in-stack (e.g., a plug of glass wool inserted into the end of the probe) or heated out-stack (e.g., as described in Method 5), to remove particular matter.

When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

2.1.2 Condenser. The condenser consists of four impingers connected in series with ground glass, leak-free fittings or any similarly leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 centimeter (½ inch) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator.

The first two impingers shall contain known volumes of water, the third shall be empty, and the fourth shall contain a known weight of 6- to 16-mesh indicating type silica gel, or equivalent desiccant. If the silica gel has been previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. A thermometer, capable of measuring temperature to within 1° C (2° F), shall be placed at the outlet of the fourth impinger, for monitoring purposes.

Alternatively, any system may be used (subject to the approval of the Administrator) that cools the sample gas stream and allows measurement of both the water that has been condensed and the moisture leaving the condenser, each to within 1 ml or 1 g. Acceptable means are to measure the condensed water, either gravimetrically or volumetrically, and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures, or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap, with exit gases kept below 20° C (68° F), and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump, to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

2.1.3 Cooling System. An ice bath container and crushed ice or equivalent are used to aid in condensing moisture.

2.1.4 Metering System. This system includes a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter capable of measuring volume to within 2 percent, and related equipment as shown in Figure 4-1. Other metering systems, capable of maintaining a constant sampling rate and determining sample gas volume, may be used, subject to the approval of the Administrator.

2.1.5 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg) may be used. In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.6 Graduated Cylinder and/or Balance. These items are used to measure condensed water and moisture caught in the silica gel to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. These balances are suitable for use here.

2.2 Procedure. The following procedure is written for a condenser system (such as the impinger system described in Section 2.1.2) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

2.2.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used in all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Administrator. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Place known volumes of water in the first two impingers. Weigh and record the

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weight of the silica gel to the nearest 0.5 g. and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

2.2.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m³/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

2.2.3 Set up the sampling train as shown in Figure 4-1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of about 120° C (248° F), to prevent water condensation ahead of the condenser; allow time for the temperatures to stabilize. Place crushed ice in the ice bath container. It is recommended, but not required, that a leak check be done, as follows: Disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder) and pull a 380 mm (15 in.) Hg vacuum; a lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m³/min (0.02 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

2.2.4 During the sampling run, maintain a sampling rate within 10 percent of con-

stant rate, or as specified by the Administrator. For each run, record the data required on the example data sheet shown in Figure 4-2. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point, at least once during each time increment.

2.2.5 To begin sampling, position the probe tip at the first traverse point. Immediately start the pump and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less 20° C (68° F) at the silica gel outlet.

2.2.6 After collecting the sample, disconnect the probe from the filter holder (or from the first impinger) and conduct a leak check (mandatory) as described in Section 2.2.3. Record the leak rate. If the leakage rate exceeds the allowable rate, the tester shall either reject the test results or shall correct the sample volume as in Section 6.3 of Method 5. Next, measure the volume of the moisture condensed to the nearest ml. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4-3) and calculate the moisture percentage, as described in 2.3 below.

2.3 Calculations. Carry out the following calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

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FIGURE 4-2—FIELD MOISTURE DETERMINATION REFERENCE METHOD

Plant
Location
Operator
Date
Run No
Ambient temperature
Barometric pressure
Probe length m (ft)

SCHEMATIC OF STACK CROSS SECTION

Traverse point number	Sampling time (θ), min	Stack temperature °C (°F)	Pressure differential across orifice meter ΔH mm (in.) H₂O	Meter reading gas sample volume m³ (ft³)	ΔV_m m³ (ft³)	Gas Sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger °C (°F)
						Inlet (T_m_) °C (°F)	Outlet (T_m_) °C (°F)	
Total Average					Avg	Avg	Avg	

FIGURE 4-3—ANALYTICAL DATA—REFERENCE METHOD

	Impinger volume ml	Silica gel weight g
Final	..	
Initial		..
Difference	..	..

2.3.1 Nomenclature.

B_{ws} = Proportion of water vapor, by volume, in the gas stream.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg) (m³)/(g-mole) (°K) for metric units and 21.85 (in. Hg) (ft³)/(lb-mole) (°R) for English units.

T_m = Absolute temperature at meter, °K (°R).

T_{std} = Standard absolute temperature, 293° K (528°R).

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

ΔV_m = Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$ = Volume of water vapor condensed corrected to standard conditions, scm (scf).

$V_{wsg(std)}$ = Volume of water vapor collected in silica gel corrected to standard conditions, scm (scf).

V_f = Final volume of condenser water, ml.

V_i = Initial volume, if any, of condenser water, ml.

W_f = Final weight of silica gel or silica gel plus impinger, g.

W_i = Initial weight of silica gel or silica gel plus impinger, g.

Y = Dry gas meter calibration factor.

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

2.3.2 Volume of water vapor condensed.

$$V_{wc(std)} = \frac{(V_f - V_i)\rho_w R T_{std}}{P_{std} M_w}$$

$$= K_1 (V_f - V_i)$$

Equation 4-1
where:
K_1 = 0.001333 m³/ml for metric units
= 0.04707 ft³/ml for English units

2.3.3 Volume of water vapor collected in silica gel.

$$V_{wsg(std)} = \frac{(W_f - W_i) R T_{std}}{P_{std} M_w}$$

$$= K_2 (W_f - W_i)$$

Equation 4-2
where:
K_2 = 0.001335 m³/g for metric units
= 0.04715 ft³/g for English units

2.3.4 Sample gas volume.

$$V_{m(std)} = V_m Y \frac{(P_m)(T_{std})}{(P_{std})(T_m)}$$

$$= K_3 Y \frac{V_m P_m}{T_m}$$

Equation 4-3
where:
K_3 = 0.3858 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units

NOTE: If the post-test leak rate (Section 2.2.6) exceeds the allowable rate, correct the value of V_m in Equation 4-3, as described in Section 6.3 of Method 5.

2.3.5 Moisture Content.

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}}$$

Equation 4-4

NOTE: In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the saturated conditions (see Section 1.2), and another based upon the results of the impinger analysis. The lower of these two values of B_{ws} shall be considered correct.

2.3.6 Verification of constant sampling rate. For each time increment, determine the ΔV_m. Calculate the average. If the value

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for any time increment differs from the average by more than 10 percent, reject the results and repeat the run.

3 Approximation Method

The approximation method described below is presented only as a suggested method (see Section 1.2).

3.1 Apparatus.

3.1.1 Probe.—Stainless steel glass tubing, sufficiently heated to prevent water condensation and equipped with a filter (either instack or heated out-stack) to remove particulate matter. A plug of glass wool, inserted into the end of the probe, is a satisfactory filter.

3.1.2 Impingers. Two midget impingers, each with 30 ml capacity, or equivalent.

3.1.3 Ice Bath. Container and ice, to aid in condensing moisture in impingers.

3.1.4 Drying Tube. Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

3.1.5 Valve. Needle valve, to regulate the sample gas flow rate.

3.1.6 Pump. Leak-free, diaphragm type, or equivalent, to pull the gas sample through the train.

3.1.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2%, and calibrated over the range of flow rates and conditions actually encountered during sampling.

3.1.8 Rate Meter. Rotameter, to measure the flow range from 0 to 3 lpm (0 to 0.11 cfm).

3.1.9 Graduated Cylinder 25 ml.

3.1.10 Barometer. Mercury, aneroid, or other barometer, as described in Section 2.1.5 above.

3.1.11 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge, to be used for the sampling leak check.

3.2 Procedure.

3.2.1 Place exactly 5 ml distilled water in each impinger.

Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet; then, plug the probe inlet and pull a vacuum of at least 250 mm Hg (10 in. Hg). Note, the time rate of change of the dry gas meter dial; alternatively, a rotameter (0–40 cc/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak rate not in excess of 2 percent of the average sampling rate is acceptable.

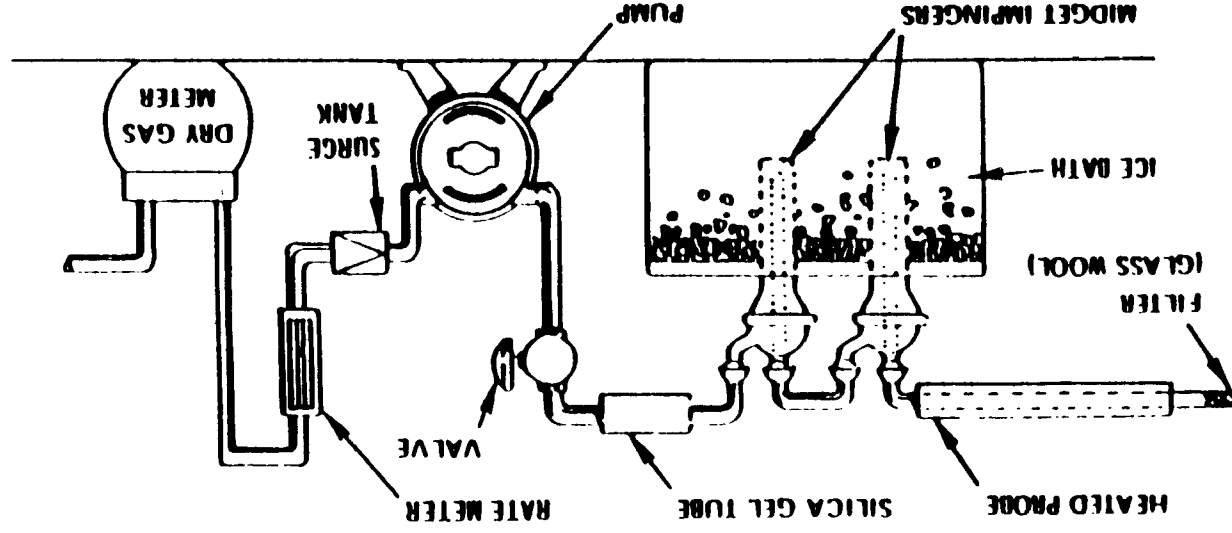Note: Carefully release the probe inlet plug before turning off the pump.

Figure 4 4. Moisture sampling train - approximation method.

Location ___ ___ Comments
Test
Date
Operator ___ ___ ....
Barometric pressure ___ ...

Clock time	Gas volume through meter (Vm), m³ (ft³)	Rate meter setting m³/ min (ft³/ min)	Meter temperature, C (°F)
	·		

3.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 2 lpm (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft³) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4-5.

3.2.3 After collecting the sample, combine the contents of the two impingers and measure the volume to the nearest 0.5 ml.

3.3 Calculations. The calculation method presented is designed to estimate the moisture in the stack gas; therefore, other data which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content, for the purpose of determining isokinetic sampling rate settings.

3.3.1 Nomenclature.

B_{wm} = Approximate proportion, by volume, of water vapor in the gas stream leaving the second impinger, 0.025.

B_{ws} = Water vapor in the gas stream, proportion by volume.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter.

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 (mm Hg) (m³)/(g-mole) (°K) for metric units and 21.85 (in. Hg) (ft³/lb-mole) (°R) for English units.

T_m = Absolute temperature at meter, °K (°R).

T_{std} = Standard absolute temperature, 293° K (528° R).

V_f = Final volume of impinger contents, ml.
V_i = Initial volume of impinger contents, ml.

V_m = Dry gas volume measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{wc(std)}$ = Volume of water vapor condensed, corrected to standard conditions, scm (scf).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

Y = Dry gas meter calibration factor.

3.3.2 Volume of water vapor collected.
where:

$$V_w = \frac{(V_f - V_i)\rho_w R T_{std}}{P_{std} M_w}$$

$$= K_1(V_f - V_i)$$

Equation 4-5
K_1 = 0.001333 m³/ml for metric units
= 0.04707 ft³/ml for English units.
3.3.3 Gas volume.

$$V_{m(std)} = V_m \left(\frac{P_m}{P_{std}}\right) \left(\frac{T_{std}}{T_m}\right)$$

$$= K_2 \frac{V_m P_m}{T_m}$$

Equation 4-6

where:
K_2 = 0.3858 °K/mm Hg for metric units
= 17.64 °R/in. Hg for English units
3.3.4 Approximate moisture content.

$$B_{ws} = \frac{V_{wc}}{V_{wc} + V_{m(std)}} + B_{wm}$$

$$= \frac{V_{wc}}{V_{wc} + V_{m(std)}} + (0.025)$$

Equation 4-7

4. Calibration

4.1 For the reference method, calibrate equipment as specified in the following sections of Method 5: Section 5.3 (metering system); Section 5.5 (temperature gauges); and Section 5.7 (barometer). The recommended leak check of the metering system (Section 5.6 of Method 5) also applies to the reference method. For the approximation method, use the procedures outlined in Section 5.1.1 of Method 6 to calibrate the me-

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ur ng system. and the procedure of Method
5 Sect on 5.7 to calibrate the barometer

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METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

1.1 Principle. Particulate matter is with-
drawn isokinetically from the source and
collected on a glass fiber filter maintained
at a temperature in the range of $120 \pm 14°$ C
$(248 \pm 25°$ F) or such other temperature as
specified by an applicable subpart of the
standards or approved by Administrator.

U.S. Environmental Protection Agency for
a particular application. The particulate
mass. which includes any material that con-
denses at or above the filtration tempera-
ture. is determined gravimetrically after re-
moval of uncombined water.

1.2 Applicability. This method is applica-
ble for the determination of particulate
emissions from stationary sources.

2. *Apparatus*

2.1 Sampling Train. A schematic of the
sampling train used in this method is shown
in Figure 5-1. Complete construction details
are given in APTD-0581 (Citation 2 in Sec-
tion 7); commercial models of this train are
also available. For changes from APTD-
0581 and for allowable modifications of the
train shown in Figure 5-1. see the following
subsections.

The operating and maintenance proce-
dures for the sampling train are described in
APTD-0576 (Citation 3 in Section 7). Since
correct usage is important in obtaining valid
results. all users should read APTD-0576
and adopt the operating and maintenance
procedures outlined in it. unless otherwise
specified herein. The sampling train con-
sists of the following components:

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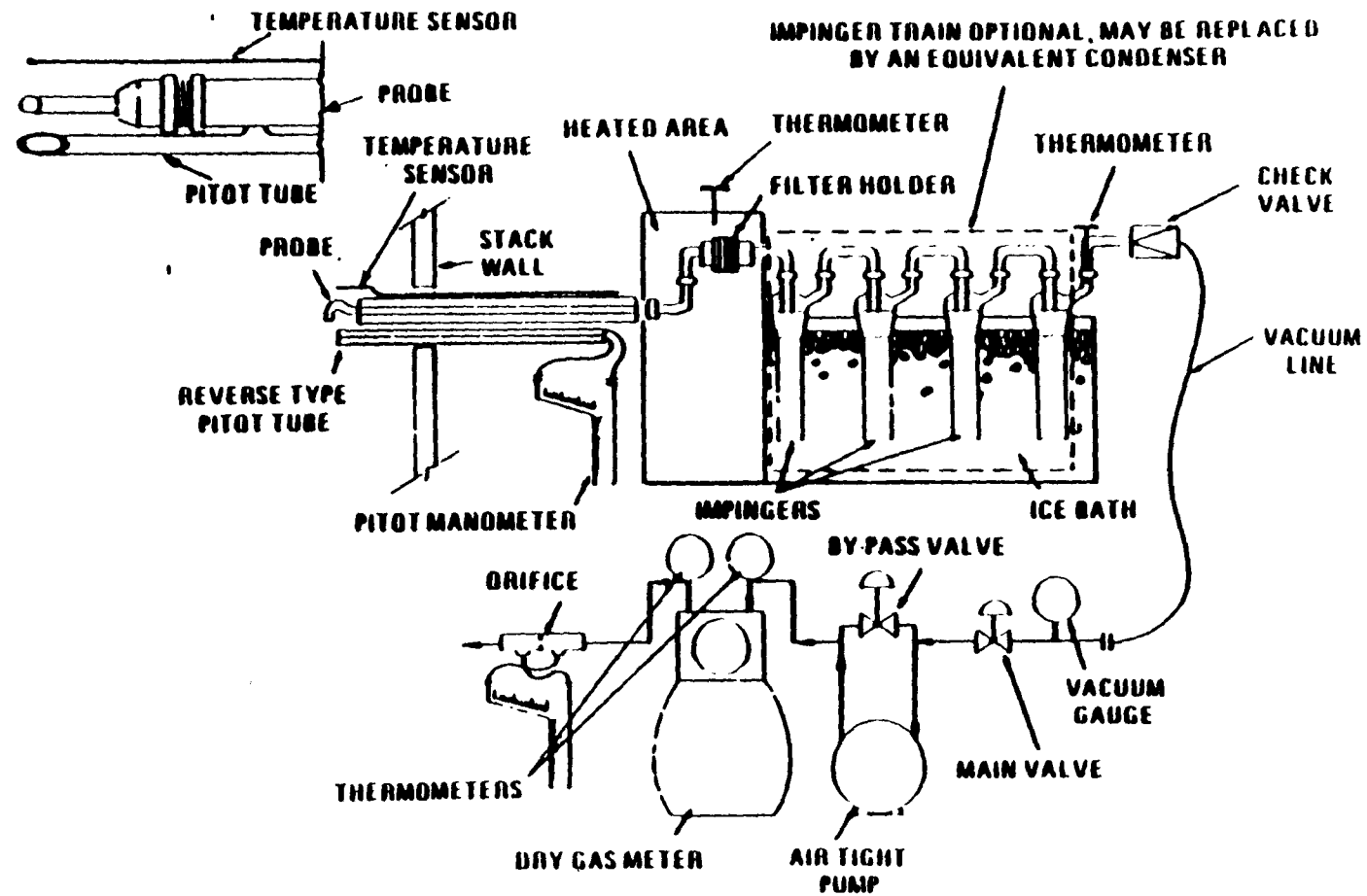
Figure 5 1 Particulate sampling train

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be used, subject to the approval of the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (⅛ to ½ in.)—or larger if higher volume sampling trains are used—inside diameter (ID) nozzles in increments of 0.16 cm (¹⁄₁₆ in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable.

Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480° C (900° F) quartz liners shall be used for temperatures between 480 and 900° C (900 and 1,650° F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate is 820° C (1,508° F), and for quartz it is 1,500° C (2,732° F).

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825,[1] or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high

· Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

2.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, Viton) may be used, subject to approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder during sampling of 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3° C (5.4° F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

2.1.7 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 4.1.3), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A thermometer, capable of measuring temperature to within 1° C (2° F) shall be placed at the outlet of the fourth impinger for monitoring purposes.

Alternatively, any system that cools the sample gas stream and allows measurement

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of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample has stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20° C (68° F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE: If a determination of the particulate matter collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

2.1.8 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APDT-0576 may be used provided that the specifications of this method are met.

2.1.9 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.10 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

2.2 Sample Recovery. The following items are needed.

2.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 Wash Bottles—Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable or use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Airtight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

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2.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

2.2 Analysis. For analysis, the following equipment is needed.

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Balance. To measure to within 0.5 g.

2.3.5 Beakers. 250 ml.

2.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

2.3.7 Temperature Gauge. To measure the temperature of the laboratory environment.

3. Reagents

3.1 Sampling. The reagents used in sampling are as follows:

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71 (Reapproved 1978) (incorporated by reference—see § 60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO₂ or SO₃, the filter material must be of a type that is unreactive to SO₂ or SO₃. Citation 10 in Section 7 Bibliography, may be used to select the appropriate filter.

3.1.2 Silica Gel. Indicating type. 6 to 16 mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.3 Water. When analysis of the material caught in the impingers is required, distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 Crushed Ice.

3.1.5 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

3.2 Sample Recovery. Acetone-reagent grade, <0.001 percent residue, in glass bottles—is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (<0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of

acetone used be subtracted from the sample weight.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 Acetone. Same as 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation. All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in the impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20±5.6° C (68±10° F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 0.5 mg change from previous weighing, record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105° C (220° F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack

gas dry molecular weight, as described in Method 2. Section 3 6. if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors. The sampling time at each point shall be the same.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the

filter. Check the filter for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260° C (500° F) and an asbestos string gasket when temperatures are higher. See APTD-0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Set up the train as in Figure 5-1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m³/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and

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APPENDIX C

MEASUREMENT OF TOTAL HYDROCARBONS IN STACK GASES FROM HAZARDOUS WASTE INCINERATORS, BOILERS, AND INDUSTRIAL FURNACES

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HAZARDOUS WASTE INCINERATORS, BOILERS, AND INDUSTRIAL FURNACES

1.0 Applicability and Principle

1.1 Applicability.

This method applies to the measurement of total hydrocarbons as a surrogate
measure for total gaseous organic concentration in the combustion gas
stream. The concentration is expressed in terms of propane by volume (ppmv).

1.2 Principle.

A gas sample is extracted from the source through a sample line, and gas
conditioning system to a flame ionization detector (FID). Results are
reported as volume concentration equivalents of the propane.

2.0 Definitions

2.1 Continuous Emission Monitoring System (CEMS).

The CEMS is comprised of all the equipment used to generate data and includes
the sample extraction and transport hardware, sample conditioning system, the
FID analyzer(s), and the data recording/processing hardware (and software).

2.2 Continuous.

A continuous monitor is one in which the sample to be analyzed passes the
measurement section of the analyzer without interruption and which evaluates
the detector response to the sample at least once each 15 s and records the
average of these observations each and every minute.

The hourly rolling average is the arithmetic mean of sixty (60) most recent 1-min average values recorded by the continuous monitoring system.

2.3 Span Value.

The upper limit of the gas concentration measurement range. For most incinerators a 50-ppm propane span is appropriate. Higher span values may be necessary if the THC emission spikes are several and higher. In such cases a 100-ppm propane span should be adequate. For convenience, the span value should correspond to 100 percent of the recorder scale.

2.4 Calibration Gas.

A known concentration of a gas in an appropriate diluent gas.

2.5 Zero Drift.

The difference in the measurement system response to a zero level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.6 Calibration Drift.

The difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

2.7 Response Time.

The time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

2.8 Calibration Error.

The difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.

3.0 Monitoring System Types

There are two acceptable types of THC monitoring systems: heated and unheated. Heated systems maintain the temperature of the sample gas between 150° to 175°C throughout the system. This requires all system components like probe, calibration valve, filters, sample lines, pump, and the FID analyzer to be kept heated at all times such that no moisture is condensed out of the system. Unheated systems remove excess moisture from the system and pass it through a gas conditioning system kept at temperatures between 5° to 18°C (40° to 64°F) so that the moisture of the sample gas entering the FID does not exceed 2 percent.

3.1 CEMS Components.

The essential components of the measurement system are described below.

3.1.1 FID Analyzer.

That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

3.1.2 Data Recorder.

That portion of the system that computes the hourly rolling averages, displays and records a permanent record of the measurement values. Combinations of gauges, strip chart recorders, data loggers, and computers are examples. The minimum data recording requirement is one measurement value per min.

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3.1.3   Sample Probe.

Stainless steel, or equivalent, three-hole rake type. Sample holes shall be 4 mm in diameter or smaller and located at 16.7, 50, and 83.3 percent of the equivalent stack diameter. Alternatively, a single opening probe may be used so that a gas sample is collected from the centrally located 10 percent area of the stack cross section.

3.1.4   Sample Line.

Stainless steel or Teflon* tubing to transport the sample gas to the analyzer.

3.1.5   Calibration Valve Assembly.

A three-way valve assembly to direct the zero and calibration gases to the analyzers is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

3.2   Sample Conditioning System for Unheated Analyzer.

A sample conditioning system consisting of particulate filter(s), chiller(s), and condenser(s) shall be provided to remove particulates and excess moisture from the sample gas before it reaches the FID. Particulates removal prevents damage to the pump and the sampling valves and avoids full or partial blockage of sampling lines which could result in decreased flow to the FID. The particulate filters may be of in-stack or out-of-stack type and should be heated to prevent condensation.

The moisture content of the sample gas entering the FID should not exceed 2 percent. Chillers or condensers should be provided in the system to take out the excess moisture. A temperature between 40° to 64°F should be maintained in the sample conditioning system, since the saturated moisture content of air

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* Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

at those temperatures would be 0.8 to 2 percent. The chiller/condenser syste should not allow the sample gas to bubble through the condensate to prever stripping of soluble organics out of the gas stream.

4.0 Calibration and Other Gases

Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. Preparation of calibration gases shall be done according to the procedure in Protocol No. 1 (listed in Reference 2, Section 10.0). Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value.

4.1 Fuel.

A 40 percent H_2/60 percent He or 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

4.2 Zero Gas.

High purity air with less than 0.1 parts per million by volume (ppmv) of organic material methane or carbon equivalent or less than 0.1 percent of the span value, whichever is greater.

4.3 Low-Level Calibration Gas.

Propane calibration gas (in air or nitrogen) with a concentration equivalent to 20 to 30 percent of the applicable span value.

4.4 Mid-Level Calibration Gas.

Propane calibration gas (in air or nitrogen) with a concentration equivalent to 45 to 55 percent of the applicable span value.

4.5 High-Level Calibration Gas.

Propane calibration gas (in air or nitrogen) with a concentration equivalent to 80 to 90 percent of the applicable span value.

5.0 Measurement System Performance Specifications

5.1 Zero Drift.

Less than ±3 percent of the span value.

5.2 Calibration Drift.

Less than ±3 percent of the span value.

5.3 Calibration Error.

Less than ±5 percent of the calibration gas value.

6.0 Pretest Preparations

6.1 Selection of Sampling Site.

The location of the sampling site is generally specified by the applicable regulation or purpose of the test, i.e., exhaust stack, inlet line, etc. The sample port shall be located at least 1.5 m or 2 equivalent diameters upstream of the gas discharge to the atmosphere.

6.2 Location of Sample Probe.

Install the sample probe so that the probe is centrally located in the stack, pipe, or duct and is sealed tightly at the stack port connection.

6.3 Measurement System Preparation.

Prior to the emission test, assemble the measurement system following the manufacturer's written instructions in preparing the sample interface and the organic analyzer. Make the system operable.

6.4 Calibration Error Test.

Immediately prior to the test series (within 2 h of the start of the test) introduce zero gas and high-level calibration gas at the calibration valve assembly. Adjust the analyzer output to the appropriate levels, if necessary. Calculate the predicted response for the low-level and mid-level gases based on a linear response line between the zero and high-level responses. Then introduce low-level and mid-level calibration gases successively to the measurement system. Record the analyzer responses for low-level and mid-level calibration gases and determine the differences between the measurement system responses and the predicted responses. These differences must be less than 5 percent of the respective calibration gas value. If not, the measurement system is not acceptable and must be replaced or repaired prior to testing. No adjustments to the measurement system shall be conducted after the calibration and before the drift check (Section 7.3). If adjustments are necessary before the completion of the test series, perform the drift checks prior to the required adjustments and repeat the calibration following the adjustments. If multiple electronic ranges are to be used, each additional range must be checked with a mid-level calibration gas to verify the multiplication factor.

6.5 Response Time Test.

Introduce zero gas into the measurement system at the calibration valve assembly. When the system output has stabilized, switch quickly to the high-level calibration gas. Record the time from the concentration change to the measurement system response equivalent to 95 percent of the step change. Repeat the test three times and average the results.

7.0 Emissions Measurement Test Procedure

7.1 Organic Measurement.

Begin sampling at the start of the test period, recording the time and any required process information as appropriate. In particular, note on the recording chart periods of process interruption or cyclic operation.

7.2 Drift Determination.

Immediately following the completion of the test period and hourly during the test period, reintroduce the zero and mid-level calibration gases, one at a time, to the measurement system at the calibration valve assembly. (Make no adjustments to the measurement system until after both the zero and calibration drift checks are made.) Record the analyzer response. If the drift values exceed the specified limits, invalidate the test results preceding the check and repeat the test following corrections to the measurement system. Alternatively, recalibrate the test measurement system as in Section 6.4 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period).

8.0 Organic Concentration Calculations

Determine the average organic concentration in terms of ppmv propane. The average shall be determined by the integration of the output recording over the period specified in the applicable regulation.

9.0 Reporting of Total Hydrocarbon Levels

THC levels from the trial burn will be reported as ppmv propane and need to be converted to the mg/s units used for the de minimis THC values. This conversion is accomplished with the following equation:

$$\text{THC, mg/s} = (\text{THC ppmv propane}) \times (\text{Stack gas flow}) \times 2.8 \times 10^{-2}$$

where:

- THC = concentration as measured by the THC method, ppm propane,

- Stack gas flow = in dry standard cubic meters per minute measured by EPA Reference Method 5 (or Modified EPA Method 5) during the ORE trial burn, and

- The constant factor 2.8×10^{-2} is derived from the following equation: $\dfrac{(6.9 \times 10^{-4})\ (45.3)}{(0.75)\ (1.5)}$

where:

- 6.9×10^{-4} = factor to convert units,

- 45.3 = weighted average molecular weight of the generic list of carcinogenic and noncarcinogenic compounds, g/g-mole,

- 1.5 = ratio of response of propane (3.0) to the weighted average response of the generic list of compounds (1.95) to a flame ionization detector, dimensionless, and

- 0.75 = dimensionless factor to adjust the measured THC for the potential loss of heavy organics in the sampling system. This factor is based on a conservative analysis of the fraction of the total organic mass emitted from combustion devices that is nonvolatile and, therefore, has potential to condense or be adsorbed in the sampling system precluding detection by the THC monitor.

10.0 Bibliography

1. *Measurement of Volatile Organic Compounds—Guideline Series*, U.S Environmental Protection Agency, Research Triangle Park, North Carolina Publication No. EPA-450/2-78-041, pp. 46-54 (June 1978).

2. *Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emissions Monitors (Protocol No. 1)*, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Research Triangle Park, North Carolina (June 1978).

3. *Gasoline Vapor Emission Laboratory Evaluation—Part 2*, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EMB Report No. 75-GAS-6 (August 1975).

APPENDIX D

DRAFT METHODS FOR THE DETERMINATION OF HCl EMISSIONS FROM MUNICIPAL AND HAZARDOUS WASTE INCINERATORS

METHOD _ _ _ _

MIDGET IMPINGER HCl/Cl₂ EMISSION SAMPLING TRAIN

DRAFT

METHOD _ _ _ _

MIDGET IMPINGER HCl/Cl₂ EMISSION SAMPLING TRAIN

1.0 SCOPE AND APPLICATION

1.1 This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl₂, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators and municipal waste combustors. The collected samples are analyzed using Method XXXX. This method is designed to collect HCl/Cl₂ in their gaseous forms. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter (e.g., HCl dissolved in water droplets) must be sampled using an isokinetic HCl/Cl₂ sampling train (see Method XXXX).

2.0 SUMMARY OF METHOD

2.1 An integrated gas sample is extracted from the stack and passes through a particulate filter, acidified water, and finally through an alkaline solution. The filter serves to remove particulate matter such as chloride salts which could potentially react and form analyte in the absorbing solutions. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride (Cl⁻) ions. The Cl₂ gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H⁺), Cl⁻, and hypochlorous acid (HClO). The Cl⁻ ions in the separate solutions are measured by ion chromatography (Method XXXX).

3.0 INTERFERENCES

3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferent for HCl is diatomic chlorine (Cl₂) gas which disproportionates to HCl and hypochlorous acid (HOCl) upon dissolution in water. Cl₂ gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl₂ with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl₂ results in a positive bias of 3.4% in the HCl measurement.

4.0 APPARATUS AND MATERIALS

4.1 Sampling Train. The sampling train is shown in Figure 1 and component parts are discussed below.

4.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) inside diameter, with a heating system to prevent condensation. When the concentration of alkaline particulate matter in the emissions is high, a 3/8-in. (9-mm) inside diameter Teflon elbow should be attached to the inlet of the probe; a 1-in. (25-mm) length of Teflon tubing with a 3/8-in.

(9-mm) inside diameter should be attached at the open end of the elbow to permit the opening of the probe to be turned away from the gas stream, thus reducing the amount of particulate entering the train. When high concentrations of particulate matter are not present, the Teflon elbow is not necessary, and the probe inlet can be perpendicular to the gas stream. When sampling at locations where gas temperatures are greater than approximately 400°F, such as wet scrubber inlets, glass or quartz elbows. must be used. In no case should a glass wool plug be used to remove particulate matter; use of such a filtering device could result in a bias in the data.[1] Instead, a Teflon filter should be used as specified in Section 4.1.5.

4.1.2 Three-way stopcock. A borosilicate, three-way glass stopcock with a heating system to prevent condensation. The heated stopcock should connect directly to the outlet of the probe and filter assembly and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

4.1.3 Impingers. Five 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for extended sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

4.1.4 Mae West impinger or drying tube. Mae West design impinger (or drying tube, if a moisture determination is not to be conducted) filled with silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump.

4.1.5 Sample line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

4.1.6 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for the elevation differences between the weather station and sampling point shall be applied at rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

4.1.7 Purge pump, purge line, drying tube, needle valve, and rate meter. Pump capable of purging sample probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter, 0 to 5 liters/min.

4.1.8 Metering system. The following items comprise the metering system which is identical to that used for EPA Method 6 (see Reference 5).

4.1.8.1 Valve. Needle valve, to regulate sample gas flow rate.

4.1.8.2 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through train. Install a small surge tank between the pump and the rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

4.1.8.3 Rate meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of selected flow rate of 2 liters/min.

4.1.8.4 Volume meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions encountered during sampling, and equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within 3°C (5.4°F).

4.1.8.5 Vacuum gauge. At least 760 mm Hg (30 in. Hg) gauge to be used for leak check of the sampling train.

4.2 Sample Recovery.

4.2.1 Wash bottles. Polyethylene or glass, 500 ml or larger, two.

4.2.2 Storage bottles. Glass, with Teflon-lined lids, 100 ml, to store impinger samples (two per sampling run).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see Method XXXX).

5.3 Sulfuric acid (0.1 $\underline{N}$), H_2SO_4. Used as the HCl absorbing reagent. To prepare 100 mL, slowly add 0.28 mL of concentrated H_2SO_4 to about 90 mL of water while stirring, and adjust the final volume to 100 mL using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see Method XXXX).

5.4 Sodium hydroxide (0.1 $\underline{N}$), NaOH. Used as the Cl_2 absorbing reagent. To prepare 100 mL, dissolve 0.40 g of solid NaOH in about 90 mL of water and adjust the final volume to 100 mL using additional water. Shake well to mix

the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see Method XXXX).

5.5 Filter. 25-mm Teflon mat Pallflex^R TX40HI75 or equivalent. Locate in a glass or quartz filter holder in a filter box heated to 250°F.

5.6 Stopcock grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

5.7 Silica gel. Indicating type, 6- to 16-mesh. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection is described in this method. The analytical procedures are described in Method XXXX.

6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

7.0 PROCEDURE

7.1 Calibration. Section 3.5.2 of EPA's Quality Assurance Handbook, Volume III (Reference 4) may be used as a guide for these operations.

7.1.1 Dry Gas Metering System.

7.1.1.1 Initial calibration. Before its initial use in the field, first leak check the metering system (sample line, drying tube, if used, vacuum gauge, needle valve, pump, rate meter, and dry gas meter) as follows: plug the inlet end of the sampling line, pull a vacuum of 250 mm (10 in.) Hg, plug off the outlet of the dry gas meter, and turn off the pump. The vacuum should remain stable for 30 seconds. Carefully release the vacuum from the system by slowly removing the plug from the sample line inlet. Remove the sampling line (and drying tube, if applicable), and connect the dry gas metering system to a appropriately sized wet test meter (e.g., 1 liter per revolution). Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, with both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

7.1.1.2 Post-test calibration check. After each field test series, conduct a calibration check as in Section 7.1.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three or more revolutions of the dry gas meter may be used, (c) only two independent runs need to be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in Section 7.1.1.1), the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as Section 7.1.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

7.1.2 Thermometer(s). Prior to each field test, calibrate against mercury-in-glass thermometers at ambient temperature. If the thermometer being calibrated reads within 2°C (2.6°F) of the mercury-in-glass thermometer, it is acceptable. If not, adjust the thermometer or use an appropriate correction factor.

7.1.3 Rate meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

7.1.4 Barometer. Prior to each field test, calibrate against a mercury barometer. The field barometer should agree within 0.1 in. Hg with the mercury barometer. If it does not, the field barometer should be adjusted.

7.2 Sampling.

7.2.1 Preparation of collection train. Prepare the sampling train as follows: The first or knockout impinger should have a shortened stem and be left empty to condense moisture in the gas stream. The next two midget impingers should each be filled with 15 mL of 0.1 N H_2SO_4, and the fourth and fifth impingers should each be filled with 15 mL of 0.1 N NaOH. Place a fresh charge of silica gel, or equivalent, in the Mae West impinger (or the drying tube). Connect the impingers in series with the knockout impinger first, followed by the two impingers containing the acidified reagent and two impingers containing the alkaline reagent, and the Mae West impinger containing the silica gel. If the moisture will be determined, weigh the impinger assembly to the nearest $\pm$ 0.5 g and record the weight.

7.2.2 Leak check procedures. Leak check the probe and three-way stopcock prior to inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Place the probe in the stack at the sampling location, and adjust the filter heating system to 250°F and the probe and stopcock heating systems to a temperature sufficient to prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to

the last impinger and the needle valve. Upon completion of a sampling run, remove the probe from the stack and leak check as described above If a leak has occurred, the sampling run must be voided. Alternatively, the portion of the train behind the probe may be leak checked between multiple runs at the same site as follows: Close the stopcock to the first impinger (see Figure 1A), and turn on the sample pump. Pull a vacuum of at least 250 mm Hg (10 in. Hg), turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Release the vacuum on the impinger train by turning the stopcock to the vent position to permit ambient air to enter (see Figure 1B). If this procedure is used, the full train leak check described above must be conducted following the final run and all preceding sampling runs voided if a leak has occurred.

7.2.3 Purge procedure. Immediately prior to sampling, connect the purge line to the stopcock and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes prior to sampling.

7.2.4 Sample collection. Turn on sample pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate within 10 percent during the entire sampling run. Take readings of the dry gas meter, the dry gas meter temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of two hours is recommended. However, if the expected condensate catch for this sampling run duration will exceed the capacity of the sampling train, (1) a larger knockout impinger may be used or (2) two sequential one-hour runs may be conducted. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak check as described in Section 7.2.2.

7.3 Sample recovery. Following sampling, disconnect the impinger train from the remaining sampling equipment at the inlet to the knockout impinger and the outlet to the last impinger. If performing a moisture determination, wipe off any moisture on the outside of the train and any excess silicone grease at the inlet and outlet openings; weigh the train to the nearest 0.5 g and record this weight. Then disconnect the impingers from each other. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two 0.1 N H_2SO_4 impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle. The contents of the impingers and connecting glassware from the second set of impingers (containing the 0.1 N NaOH) should be recovered in a similar manner if a Cl_2 analysis is desired. The sample bottle should be sealed, shaken to mix, and labeled; the fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Save portions of the 0.1 N H_2SO_4 and 0.1 N NaOH used as impinger reagents as reagent blanks. Take 50 ml of each and place in separate leak-free storage bottles. Label and mark the fluid levels as previously described.

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7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

7.4.1 Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume.

M_v = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Average dry gas meter absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293°K (528oR).

V_{lc} = Total volume of liquid collected in impingers and silica gel, mL (equivalent to the difference in weight of the impinger train before and after sampling, 1 mg = 1 mL).

V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

Y = Dry gas meter calibration factor.

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

7.4.2 Sample volume, dry basis, corrected to standard conditions. Calculate as described below:

$$V_{m(std)} = V_m\, Y \left[\frac{T_{std}}{T_m}\right]\left[\frac{P_{bar}}{P_{std}}\right] = K_1\, Y\, \frac{V_m\, P_{bar}}{T_m} \qquad (1)$$

where:

K_1 = 0.3858°K/mm Hg for metric units.
= 17.64°R/in. Hg for English units.

7.4.3 Volume of water vapor.

$$V_{w(std)} = V_{lc} \frac{\rho_w}{M_w} \cdot \frac{RT_{std}}{P_{std}} = K_2 V_{lc}$$

where:

K_2 = 0.0013333 m^3/mL for metric units.
= 0.04707 ft^3/mL for English units.

7.4.4 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{a(std)} + V_{w(std)}} \tag{3}$$

8.0 QUALITY CONTROL

8.1 At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method XXXX.

9.0 METHOD PERFORMANCE

9.1 The in-stack detection limit for the method is approximately 0.04 ug of HCl per liter of stack gas for a 2-hour sample.

9.2 The precision and bias for measurement of HCl using this sampling protocol combined with the analytical protocol of Method XXXX have been determined. The within laboratory relative standard deviation is 6.2% and 3.2% at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at Cl_2 concentrations less than 50 ppm.

REFERENCES

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2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources," March 18, 1987.

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4. U. S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods." Publication No. EPA-600/4-77-027b, August 1977.

5. U. S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Method 6.

Figure 1 Midget impinger HCl/Cl$_2$ sampling train

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METHOD _ _ _ _

PROTOCOL FOR ANALYSIS OF SAMPLES
FROM HCl/Cl$_2$ EMISSION SAMPLING TRAINS

DRAFT

This method has been drafted based on the results of laboratory and field studies carried out under contract to the Source Branch of the Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory (QAD/AREAL), United States Environmental Protection Agency (U.S. EPA). The method is still under investigation and is subject to revision.

PROTOCOL FOR ANALYSIS OF SAMPLES
FROM HCl Cl₂ EMISSION SAMPLING TRAINS

1.0 SCOPE AND APPLICATION

1.1 This method describes the analtyical protocol for determination of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chloride (Cl_2, CAS Registry Number 7782-50-5) in stack gas emission samples collected from hazardous waste and municipal waste incinerators using the midget impinger HCl/Cl_2 sampling train (Method XXXX) or the isokinetic HCl/Cl_2 sampling train (Method XXXX).

1.2 The lower detection limit is 0.1 ug of chloride (Cl^-) per mL of sample solution. Samples with concentrations which exceed the linear range of the analytical instrumentation may be diluted.

1.3 This method is recommended for use only by analysts experienced in the use of ion chromatography and in the interpretation of ion chromatograms.

2.0 SUMMARY OF METHOD

2.1 The HCl and Cl_2 collected in the sampling train are solubilized to chloride ions (Cl^-) in the acid and alkaline absorbing solutions, respectively. Non-suppressed or suppressed ion chromatography (IC) is used for analysis of Cl^-.

3.0 INTERFERENCES

3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One likely interferent is diatomic chlorine (Cl_2) gas which disproportionates to HCl and hypochlorous acid (HOCl) upon dissolution in water. Cl_2 gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl_2 with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4% in the HCl measurement. Other interferents have not been encountered.

4.0 APPARATUS AND MATERIALS

4.1 Volumetric Flasks. Class A, various sizes.

4.2 Volumetric Pipettes. Class A, assortment, to dilute samples to calibration range of the IC.

4.3 Ion Chromatograph. Suppressed or non-suppressed. with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors. a strip chart recorder. and peak heights may be used provided the 5 percent repeatability criteria for sample analysis and the linearity criteria for the calibration curve can be met.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated. it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used. provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Sulfuric acid (0.1 $\underline{N}$), H_2SO_4. To prepare 100 mL, slowly add 0.28 mL of concentrated H_2SO_4 to about 90 mL of water while stirring, and adjust the final volume to 100 mL using additional water. Shake well to mix the solution.

5.4 Sodium hydroxide (0.1 $\underline{N}$), NaOH. To prepare 100 mL, dissolve 0.40 g of solid NaOH in about 90 mL of water and adjust the final volume to 100 mL using additional water. Shake well to mix the solution.

5.5 Reagent blank solutions. A separate blank solution of each sampling train reagent used and collected in the field (0.1 $\underline{N}$ H_2SO_4 and 0.1 $\underline{N}$ NaOH) should be prepared for analysis with the field samples. For midget impinger train sample analysis. dilute 30 mL of each reagent with rinse water collected in the field as a blank to the final volume of the samples; for isokinetic train sample analysis. dilute 200 mL to the same final volume as the field samples also using the blank sample of rinse water.

5.6 Sodium chloride. NaCl. stock standard solution. Solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which working standards can be made by appropriate volumetric dilution. Alternately, concentrated stock solutions may be produced from reagent grade NaCl that has been dried at 110°C for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. The exact Cl⁻ concentration can be calculated using the equation:

$$\text{ug Cl}^-/\text{mL} = \text{g of NaCl} \times 10^3 \times 35.453/58.44$$

Refrigerate the stock standard solutions and store no longer than one month.

5.7 Chromatographic effluent. Effective eluents for non-suppressed ion chromatography using a resin- or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution. adjusted to a pH of 4.0 using a saturated sodium borate solution. and a mM 4-dydroxy benzoate solution.

adjusted to a pH of 8.6 using 1 N sodium hydroxide. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH that contain no ions interfering with the chromatographic analysis may be used. If, using suppressed ion chromatography, the "water dip" resulting from sample injection is interfering with the chlorine peak, use a 2 mM sodium hydroxide 2.4 mM sodium bicarbonate eluent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection using the midget impinger HCl/Cl$_2$ train or the isokinetic HCl/Cl$_2$ train is described in Method XXXX or XXXX, respectively.

6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

7.0 PROCEDURE

7.1 Sample preparation for analysis. Check the liquid level in each sample, and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume can be determined from the difference between the initial and final solution levels, and this value can be used to correct the analytical results. For midget impinger train samples, quantitatively transfer each sample solution to a 100 mL volumetric flask and dilute to 100 mL with water. For isokinetic sampling train samples, quantitatively transfer each sample to a volumetric flask or graduated cylinder and dilute with water to a final volume appropriate for all samples.

7.2 Calibration of Ion Chromatograph.

7.2.1 The ion chromatographic conditions will depend on the type of analytical column used and whether suppressed or non-suppressed ion chromatography is used. An example chromatogram from a system using non-suppressed ion chromatography with a 150 mm Hamilton PRP-X100 anion column, a 2 mL/min flow rate of a 4 mL 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N sodium hydroxide, a 50 ul sample loop, and a conductivity detector set on 1.0 uS full scale is shown in Figure 1. Prior to calibration and sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl$^-$ appears in the chromatogram. If Cl$^-$ is present, repeat the load/injection procedure until no Cl$^-$ is present.

7.2.2 To prepare the calibration standards, dilute given amounts (1.0 mL or greater) of the stock standard solution to convenient volumes, using 0.1 N H$_2$SO$_4$ or 0.1 N NaOH, as appropriate. Prepare at least four standards that are within the linear range of the field samples. Inject the calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blank, and field samples. This allows compensation for any instrument drift occurring during sample analysis.

7.2.3 After injecting the standards the first time, determine the peak area or height for each standard. Using linear regression, determine the equation for the calibration curve. Compare the known concentration of each standard to its concentration predicted by the calibration equation; the percent error as calculated below should be less than or equal to 7 percent.

$$\% \text{ Error} = \frac{\text{Predicted Conc. - Known Conc.}}{\text{Known Conc.}} \times 100\%$$

7.2.4 Following analysis of the quality control sample, the reagent blanks, and the field samples, the calibration standards are injected a second time.

7.2.5 Using the average of the initial and final injections of the standards and linear regression, determine the formulas for the calibration curve to be used to calculate the field sample concentrations.

7.3 Sample analysis. Between injections of the series of calibration standards, inject in duplicate the reagent blanks and the field samples, including a matrix spike sample. Measure the areas or heights (same as done for the calibration standards) of the Cl^- peaks. Each response (peak height or area) for a duplicate injection should be within 5 percent of the average response. Use the average response to determine the concentrations of the field samples, matrix spike, and reagent blanks using the linear calibration curve. The results for a reagent blank shall not exceed 10 percent of the corresponding value for a field sample.

7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

7.4.1 Total ug HCl per sample. Calculate as described below:

$$m_{HCl} = (S-B) \times V_s \times 36.46/35.453 \tag{2}$$

where: m_{HCl} = Mass of HCl in sample, ug,

$\quad\quad$ S = Analysis of sample, ug Cl^-/mL,

$\quad\quad$ B = Analysis of reagent blank, ug Cl^-/mL,

$\quad\quad$ V_s = Volume of filtered and diluted sample, mL,

$\quad$ 36.46 = Molecular weight of HCl, ug/ug-mole, and

$\quad$ 35.453 = Atomic weight of Cl, ug/ug-mole.

7.4.2 Total ug Cl_2 per sample. Calculate as described below:

$$M_{Cl_2} = (S-B) \times V_s \times 70.90/35.45 \tag{3}$$

where:
M_{Cl_2} = Mass of Cl_2 in sample, ug,

70.90 = Molecular weight of Cl_2, ug/ug-mole, and

35.45 = Atomic weight of Cl, ug/ug-mole.

7.4.3 Concentration of HCl in the flue gas. Calculate as described below:

$$C = K \times m/V_{m(std)}$$

where:
C = Concentration of HCl or Cl_2, dry basis, mg/dscm,

$K = 10^{-3}$ mg/ug,

m = Mass of HCl or Cl_2 in sample, ug, and

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (from Method XXXX or Method XXXX).

8.0 QUALITY CONTROL

8.1 At the present time, a validated audit material does not exist for this method. However, it is strongly recommended that a quality control check sample and a matrix spike sample be used.

8.1.1 Quality control check sample. Chloride solutions of reliably known concentrations are available for purchase from the National Bureau of Standards (SRM 3182). The QC check sample should be prepared in the appropriate absorbing reagent at a concentration approximately equal to the mid range calibration standard. The quality control check sample should be injected in duplicate immediately after the calibration standards have been injected the first time. The Cl^- value obtained for the check sample using the final calibration curve should be within 10 percent of the known value for the check sample.

8.1.2 Matrix spike sample. A portion of at least one field sample should be used to prepare a matrix spike sample. Spike the sample aliquot in the range of the expected concentration. Analyze the matrix spike sample in duplicate along with the field samples. Based on the matrix spike results, determine the recovery for the spiked material. This should be within 15 percent of the known spike value.

9.0 METHOD PERFORMANCE

9.1 The lower detection limit of the analytical method is 0.1 ug of Cl^- per mL of sample solution. Samples with concentrations which exceed the linear range of the IC may be diluted.

9.2 The precision and bias for analysis of HCl using this analytical protocol have been measured in combination with the midget impinger HCl/Cl_2 train (Method XXXX) for sample collection. The within laboratory relative standard deviation is 6.2% and 3.2% at HCl concentrations of 3.9 and 15.3 ppm.

respectively. The method does not exhibit any bias for HCl when sampling at Cl₂ concentrations less than 50 ppm.
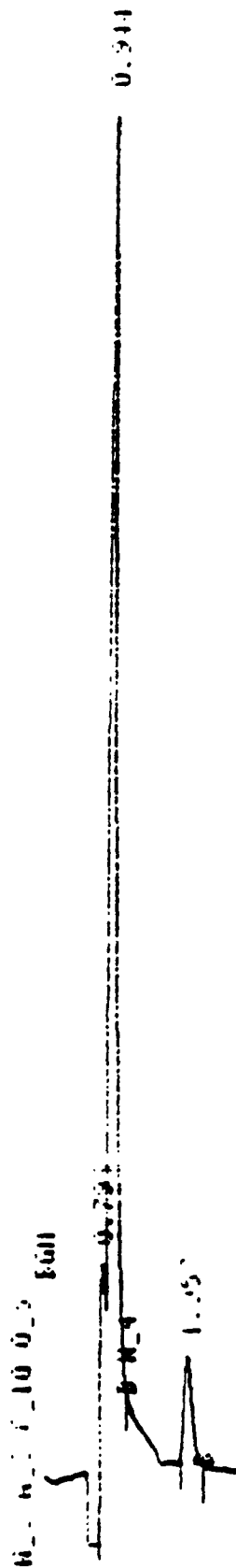
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1. Steinsberger, S. C. and J. H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U. S. Environmental Protection Agency, Office of Research and Development, Report No. ____. ____, 1989.

2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources," March 18, 1987.

3. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

Figure 1. Example ion chromatograph.

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APPENDIX E

DRAFT METALS PROTOCOL

METHODOLOGY FOR THE DETERMINATION OF METALS EMISSIONS IN EXHAUST GASES FROM HAZARDOUS WASTE INCINERATION AND SIMILAR COMBUSTION PROCESSES

1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) emissions from hazardous waste incinerators and similar combustion processes. This method may also be used for the determination of particulate emissions following the additional procedures described. Modifications to the sample recovery and analysis procedures described in this protocol for the purpose of determining particulate emissions may potentially impact the front half mercury determination.*

1.2 Principle. The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing a solution of dilute nitric acid in hydrogen peroxide in two impingers, and acidic potassium permanganate solution in two (or one) impingers. Sampling train components are recovered and digested in separate front and back half fractions. Materials collected in the sampling train are digested with acid solutions to dissolve inorganics and to remove organic constituents that may create analytical interferences. Acid digestion is performed using conventional Parr[2] Bomb or microwave digestion techniques. The nitric acid and hydrogen peroxide impinger solution, the acidic potassium permanganate impinger solution, and the probe rinse and digested filter solutions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS). Except for the permanganate solution, the remainder of the sampling

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*Field tests to date have shown that of the total amount of mercury measured by the method, only 0 to <2% was measured in the front half. Therefore, it is tentatively concluded, based on the above data, that particulate emissions may be measured by this train, without significantly altering the mercury results.

train catches are analyzed for Cr, Cd, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, lead, selenium, and thallium, if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analyses of all metals if the resulting in-stack method detection limits meet the goal of the testing program. For convenience, aliquots of each digested sample fraction can be combined proportionally for a single analytical determination. The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals including actual sample matrix effects checks.

2.   Range, Sensitivity, Precision, and Interferences

2.1   Range. For the analyses described in this methodology and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter (ug/ml) range in the analytical finish solution can be analyzed using this technique. Samples containing greater than approximately 50 ug/ml of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 ug/ml of cadmium should be diluted to that level before analysis.

2.2   Analytical Sensitivity. ICAP analytical detection limits for the sample solutions (based on SW-846, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). The actual method detection limits are sample dependent and may vary as the sample matrix may affect the limits. The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml). The detection limit for mercury by CVAAS is approximately 0.2 ng/ml. The use of GFAAS can give added sensitivity compared to the use of direct aspiration AAS for the

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following metals: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml),
Cr (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

Using (1) the procedures described in this method, (2) the analytical
detection limits described in the previous paragraph, (3) a volume of 300 ml
for the front half and 150 ml for the back half samples, and (4) a stack gas
sample volume of 1.25 m^3, the corresponding in-stack method detection limits
are presented in Table A-1 and calculated as shown:

$$\frac{A \times B}{C} = D$$

where: A = analytical detection limit, ug/ml.
       B = volume of sample prior to aliquot for analysis, ml.
       C = stack sample volume, dscm (dsm^3).
       D = in-stack detection limit, ug/m^3.

Values in Table A-1 are calculated for the front and back half and/or the total
train.

To ensure optimum sensitivity in obtaining the measurements, the
concentrations of target metals in the solutions are suggested to be at least
ten times the analytical detection limits. Under certain conditions, and with
greater care in the analytical procedure, this concentration can be as low as
approximately three times the analytical detection limit. In all cases,
repetitive analyses, method of standard additions (MSA), serial dilution, or
matrix spike addition should be used to establish the quality of the data.

Actual in-stack method detection limits will be determined based on actual
source sampling parameters and analytical results as described above. If
required, the method in-stack detection limits can be made more sensitive than
those shown in Table A-1 for a specific test by using one or more of the
following options:

o   A normal 1-hour sampling run collects a stack gas sampling volume of
    about 1.25 m^3. If the sampling time is increased and 5 m^3 are
    collected, the in-stack method detection limits would be one fourth of
    the values shown in Table A-1 (this means that with this change, the
    method is four times more sensitive than normal).

o   The in-stack detection limits assume that all of the sample is digested
    (with exception of the aliquot for mercury) and the final liquid
    volumes for analysis are 300 ml for the front half and 150 ml for the

TABLE A-1. IN-STACK METHOD DETECTION LIMITS (ug/m³) FOR TRAIN FRACTIONS USING ICAP AND AAS

Metal	Front Half Fraction 1 Probe and Filter	Back Half₁ Fraction 2 Impingers 1-3	Back Half₂ Fraction 3 Impingers 4-5	Total Train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3)*
Mercury	0.05**	0.03**	0.03**	0.11**
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5)*	9 (0.3)*		27 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

( )* Detection limit when analyzed by GFAAS.
** Detection limit when analyzed by CVAAS.
Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

back half sample. If the front half volume is reduced from 300 ml to 30 ml, the front half in-stack detection limits would be one tenth of the values shown above (ten times more sensitive). If the back half volume is reduced from 150 ml to 25 ml, the in-stack detection limits would be one sixth of the above values. Matrix effects checks are necessary on analyses of samples and typically are of greater significance for samples that have been concentrated to less than the normal sample volume. A volume less than 25 ml may not allow resolubilization of the residue and may increase interference by other compounds.

o When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front and back halves is reduced by factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive).

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o Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase limits. The front half and back half samples (Fractions 1 and 2) can be combined prior to analysis. The resultant liquid volume (excluding Fraction 3, which must be analyzed separately) is recorded. Combining the sample as described does not allow determination (whether front or back half) of where in the train the sample was captured. The in-stack method detection limit then becomes a single value for all metals except mercury, for which the contribution of Fraction 3 must be considered.

o The above discussion assumes no blank correction. Blank corrections are discussed later in this method.
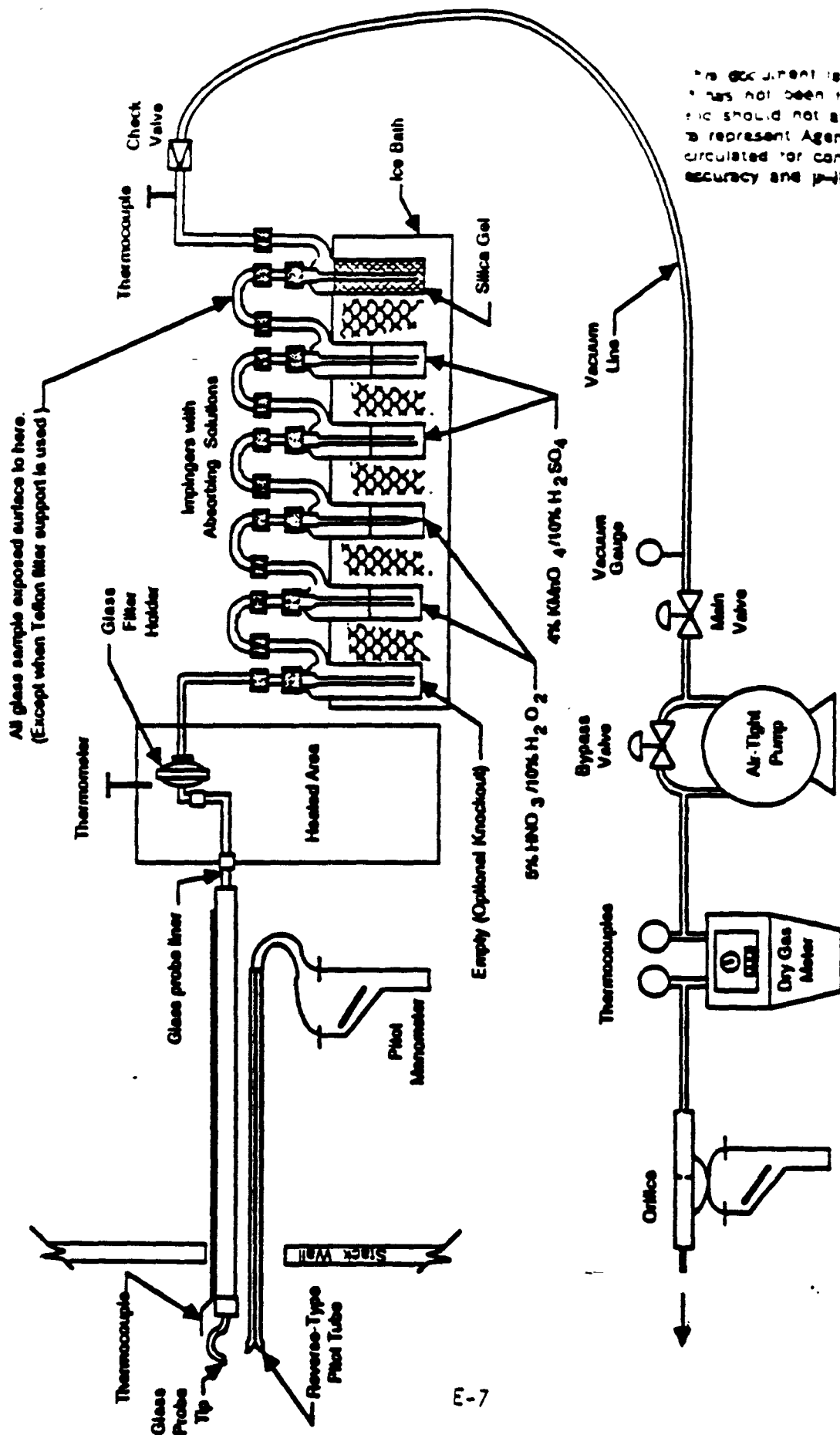
2.3 Precision. The precisions (relative standard deviation) for each metal detected in a method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese and silver were not detected in the tests; however, based on the analytical sensitivity of the ICAP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

2.4 Interferences. Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICAP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICAP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit. Refer to EPA Method 6010 (SW-846) for details on potential interferences for this method. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

3. Apparatus

3.1 Sampling Train. A schematic of the sampling train is shown in Figure A-1. It is similar to the Method 5 train. The sampling train consists of the following components.

3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 2.1.1 and 2.1.2. Glass nozzles are required unless an alternate probe tip prevents the possibility of contamination or

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Figure A-1. Schematic of multiple metals sampling train.

Check Valve

Thermocouple

Ice Bath

Silica Gel

All glass sample exposed surface to here.
(Except when Teflon filter support is used.)

Impingers with Absorbing Solutions

Glass Filter Holder

Thermometer

Heated Area

Empty (Optional Knockout)

4% KMnO$_4$/10% H$_2$SO$_4$

5% HNO$_3$/10% H$_2$O$_2$

Vacuum Line

Vacuum Gauge

Main Valve

Bypass Valve

Air-Tight Pump

Thermocouple

Dry Gas Meter

Glass probe liner

Pitot Manometer

Orifice

Thermocouple

Glass Probe Tip

Reverse-Type Pitot Tube

Stack Wall

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interference of the sample with its materials of construction. If a probe tip other than glass is used, no correction of the stack sample test results can be made because of the effect on the results by the probe tip.

3.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, Sections 2.1 and 2.2, respectively.

3.1.3 Filter Holder. Glass, same as Method 5, Section 2.1.5, except that a Teflon filter support must be used to replace the glass frit.

3.1.4 Filter Heating System. Same as Method 5, Section 2.1.6.

3.1.5 Condenser. The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The condensing system should consist of four to six impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is optional and is recommended as a water knockout trap for use during test conditions which require such a trap. The impingers to be used in the metals train are now described. When the first impinger is used as a water knockout, it shall be appropriately-sized for an expected large moisture catch and constructed generally as described for the first impinger in Method 5, Paragraph 2.1.7. The second impinger (or the first HNO_3/H_2O_2 impinger) shall also be as described for the first impinger in Method 5. The third impinger (or the impinger used as the second HNO_3/H_2O_2 impinger) shall be the same as the Greenburg Smith impinger with the standard tip described as the second impinger in Method 5, Paragraph 2.1.7. All other impingers used in the metals train are the same as the second impinger (the first HNO_3/H_2O_2 impinger) previously described in this paragraph. In summary, the first impinger should be empty, the second and third shall contain known quantities of a nitric acid/hydrogen peroxide solution (Section 4.2.1), the fourth (and fifth, if required) shall contain a known quantity of acidic potassium permanganate solution (Section 4.2.2), and the last impinger shall contain a known quantity of silica gel or equivalent desiccant. A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the water knockout impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers are removed.

3.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.8 through 2.1.10, respectively.

3.1.7 Teflon Tape. For capping openings and sealing connections on the sampling train.

3.2 Sample Recovery. Same as Method 5, Sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

3.2.1 Nonmetallic Probe-Liner and Probe-Nozzle Brushes. For quantitative recovery of materials collected in the front half of the sampling train. Description of acceptable all-Teflon component brushes to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

3.2.2 Sample Storage Containers. Glass bottles with Teflon-lined caps, 1000- and 500-ml, shall be used for $KMnO_4$-containing samples and blanks. Polyethylene bottles may be used for other sample types.

3.2.3 Graduated Cylinder. Glass or equivalent.

3.2.4 Funnel. Glass or equivalent.

3.2.5 Labels. For identification of samples.

3.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

3.3 Sample Preparation and Analysis. For the analysis, the following equipment is needed:

3.3.1 Volumetric Flasks, 100 ml, 250 ml, and 1000 ml. For preparation of standards and sample dilution.

3.3.2 Graduated Cylinders. For preparation of reagents.

3.3.3 Parr[4] Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent).

3.3.4 Beakers and Watchglasses. 250 ml beakers for sample digestion with watchglasses to cover the tops.

3.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

3.3.6 Filter Funnels. For holding filter paper.

3.3.7 Whatman 541 Filter Paper (or equivalent). For filtration of digested samples.

3.3.8 Disposable Pasteur Pipets and Bulbs.

3.3.9 Volumetric Pipets.

3.3.10 Analytical Balance. Accurate to within 0.1 mg.

3.3.11 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures.

3.3.12 Hot Plates.

3.3.13 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

3.3.13.1 Graphite Furnace Attachment. With antimony, arsenic, cadmium, lead, selenium, thallium, and hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as EPA Methods 7041 (antimony), 7060 (arsenic), 7131 (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium).

3.3.13.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10°C such that no condensation forms on the wall of the quartz cell. Same as EPA Method 7470.

3.3.14 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010.

4. Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

4.1 Sampling. The reagents used in sampling are as follows:

4.1.1 Filters. The filters shall contain less than 1.3 ug/in.^{2} of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber filters without organic binders shall be used. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D2986-71 (incorporated by reference). For particulate determination in sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3, as described in EPA Method 5. Quartz fiber filters meeting these requirements are recommended.

4.1.2 Water. To conform to ASTM Specification D1193.77, Type II (incorporated by reference). Analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

4.1.3 Nitric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.1.4 Hydrochloric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.1.5 Hydrogen Peroxide, 30 Percent (V/V).

4.1.6 Potassium Permanganate.

4.1.7 Sulfuric Acid. Concentrated.

4.1.8 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.

4.2 Pretest Preparation for Sampling Reagents.

4.2.1 Nitric Acid (HNO_3)/Hydrogen Peroxide (H_2O_2) Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add 50 ml of concentrated HNO_3 and 333 ml of 30 percent H_2O_2 to a 1000-ml volumetric flask or graduated cylinder containing approximately 500 ml of water. Dilute to volume with water. The reagent shall contain less than 2 ng/ml of each target metal.

4.2.2 Acidic Potassium Permanganate ($KMnO_4$) Absorbing Solution, 4 Percent $KMnO_4$ (W/V). Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/ml of Hg.
Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles should not be fully filled and should be vented both to relieve excess pressure and prevent explosion due to pressure buildup. Venting is highly recommended, but should not allow contamination of the sample; a No. 70-72 hole drilled in the container cap and Teflon liner has been used.

4.2.3 Nitric Acid, 0.1 N. Add 6.3 ml of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

4.2.4 Hydrochloric Acid (HCl), 8 N. Add 690 ml of concentrated HCl to a graduated cylinder containing 250 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of Hg.

4.3 Glassware Cleaning Reagents.

4.3.1 Nitric Acid, Concentrated. Fisher ACS grade or equivalent.

4.3.2 Water. To conform to ASTM Specifications D1193-77, Type II.

4.3.3 Nitric Acid, 10 Percent (V/V). Add 500 ml of concentrated HNO_3 to a graduated cylinder containing approximately 4000 ml of water. Dilute to 5000 ml with water.

4.4 Sample Digestion and Analysis Reagents.

4.4.1 Hydrochloric Acid, Concentrated.

4.4.2 Hydrofluoric Acid, Concentrated.

4.4.3 Nitric Acid, Concentrated. Baker Instra-analyzed or equivalent.

4.4.4 Nitric Acid, 10 Percent (V/V). Add 100 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.4.5 Nitric Acid, 5 Percent (V/V). Add 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Reagent shall contain less than 2 ng/ml of each target metal.

4.4.6 Water. To conform to ASTM Specifications D1193-77, Type II.

4.4.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See EPA Method 7470 for preparation.

4.4.8 Stannous Chloride.

4.4.9 Potassium Permanganate, 5 Percent (W/V).

4.4.10 Sulfuric Acid, Concentrated.

4.4.11 Nitric Acid, 50 Percent (V/V).

4.4.12 Potassium Persulfate, 5 Percent (W/V).

4.4.13 Nickel Nitrate, $Ni(NO_3)_2 \cdot 6H_2O$.

4.4.14 Lanthanum Oxide, La_2O_3.

4.4.15 AAS Grade Hg Standard, 1000 ug/ml.

4.4.16 AAS Grade Pb Standard, 1000 ug/ml.

4.4.17 AAS Grade As Standard, 1000 ug/ml.

4.4.18 AAS Grade Cd Standard, 1000 ug/ml.

4.4.19 AAS Grade Cr Standard, 1000 ug/ml.

4.4.20 AAS Grade Sb Standard, 1000 ug/ml.

4.4.21 AAS Grade Ba Standard, 1000 ug/ml.

4.4.22 AAS Grade Be Standard, 1000 ug/ml.

4.4.23 AAS Grade Cu Standard, 1000 ug/ml.

4.4.24 AAS Grade Mn Standard, 1000 ug/ml.

4.4.25 AAS Grade Ni Standard, 1000 ug/ml.

4.4.26 AAS Grade P Standard, 1000 ug/ml.

4.4.27 AAS Grade Se Standard, 1000 ug/ml.

4.4.28 AAS Grade Ag Standard, 1000 ug/ml.

4.4.29 AAS Grade Tl Standard, 1000 ug/ml.

4.4.30 AAS Grade Zn Standard, 1000 ug/ml.

4.4.31 AAS Grade Al Standard, 1000 ug/ml.

4.4.32 AAS Grade Fe Standard, 1000 ug/ml.

4.4.33 The metals standards may also be made from solid chemicals as described in EPA Method 200.7. EPA Method 7470 or Standard Methods for the Analysis of Water and Wastewater. 15th Edition. Method 303F should be referred to for additional information on mercury standards.

4.4.34 Mercury Standards and Quality Control Samples. Prepare fresh weekly a 10 ug/ml intermediate mercury standard by adding 5 ml of 1000 ug/ml mercury stock solution to a 500 ml volumetric flask; dilute to 500 ml by first adding 20 ml of 15 percent HNO_3 and then adding water. Prepare a working mercury standard solution fresh daily: add 5 ml of the 10 ug/ml intermediate standard to a 250 ml volumetric flask and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. At least six separate aliquots of the working mercury standard solution should be used to prepare the standard curve. These aliquots should contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution. Quality control samples should be prepared by making a separate 10 ug/ml standard and diluting until in the range of the calibration.

4.4.35 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as shown below.

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Cu, Fe
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 ug/ml solutions with 5 percent nitric acid. A minimum of one standard and a blank can be used to form each calibration curve. However, a

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separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve should be prepared. Suggested standard levels are 50 ug/ml for Al, 25 ug/ml for Cr and Pb, 15 ug/ml for Fe, and 10 ug/ml for the remaining elements. Standards containing less than 1 ug/ml of metal should be prepared daily. Standards containing greater than 1 ug/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.4.36 Graphite Furnace AAS Standards for Antimony, Arsenic, Cadmium, Lead, Selenium, and Thallium. Prepare a 10 ug/ml standard by adding 1 ml of 1000 ug/ml standard to a 100 ml volumetric flask. Dilute to 100 ml with 10 percent nitric acid. For graphite furnace AAS, the standards must be matrix matched; e.g., if the samples contain 6 percent nitric acid and 4 percent hydrofluoric acid, the standards should also be made up with 6 percent nitric acid and 4 percent hydrofluoric acid. Prepare a 100 ng/ml standard by adding 1 ml of the 10 ug/ml standard to a 100 ml volumetric flask and dilute to 100 ml with the appropriate matrix solution. Other standards should be prepared by dilution of the 100 ng/ml standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Quality control samples should be prepared by making a separate 10 ug/ml standard and diluting until it is in the range of the samples. Standards containing less than 1 ug/ml of metal should be prepared daily. Standards containing greater than 1 ug/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.4.37 Matrix Modifiers.

4.4.37.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(NO_3)_2 \cdot 6H_2O$ in approximately 50 ml of water in a 100 ml volumetric flask. Dilute to 100 ml with water.

4.4.37.2 Nickel Nitrate, One-tenth Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for As.

4.4.37.3 Lanthanum. Dissolve 0.5864 g of La_2O_3 in 10 ml of concentrated HNO_3 and dilute to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for Pb.

5. Procedure

5.1 Sampling. The complexity of this method is such that, to obtain reliable results, testers should be trained and experienced with the test procedures.

5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with water. All glassware should then be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled, prior to sampling.

5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

5.1.3 Preparation of Sampling Train. Follow the same general procedures given in Method 5, Section 4.1.3, except place 100 ml of the nitric acid/hydrogen peroxide solution (Section 4.2.1) in the two HNO_3/H_2O_2 impingers (normally the second and third impingers), place 100 ml of the acidic potassium permanganate solution (Section 4.2.2) in the fourth and fifth impinger, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

Several options are available to the tester based on the sampling conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers is calculated or determined to be less than 150 ml. The tester shall include two impingers containing the acidic potassium permanganate solution for the first test run, unless past testing experience at the same or similar sources has shown that only one is necessary. The last permanganate impinger may be discarded if both permanganate impingers have retained their original deep purple permanganate color. A maximum of 200 ml in each permanganate impinger (and a maximum of three permanganate impingers) may be used, if necessary, to maintain the desired color in the last permanganate impinger.

Retain for reagent blanks, 100 ml of the nitric acid/hydrogen peroxide solution and 100 ml of the acidic potassium permanganate solution. These solutions should be labeled and treated as described in Section 7. Set up the sampling train as shown in Figure A-1. If necessary to ensure leak-free sampling train connections, Teflon tape should be used instead of silicone grease to prevent contamination.

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Precaution: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent hydrogen peroxide from mixing with the acidic potassium permanganate.

5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

5.2 Sample Recovery. Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period.

The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a vacuum to form in the filter holder, thus causing the undesired result of drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination
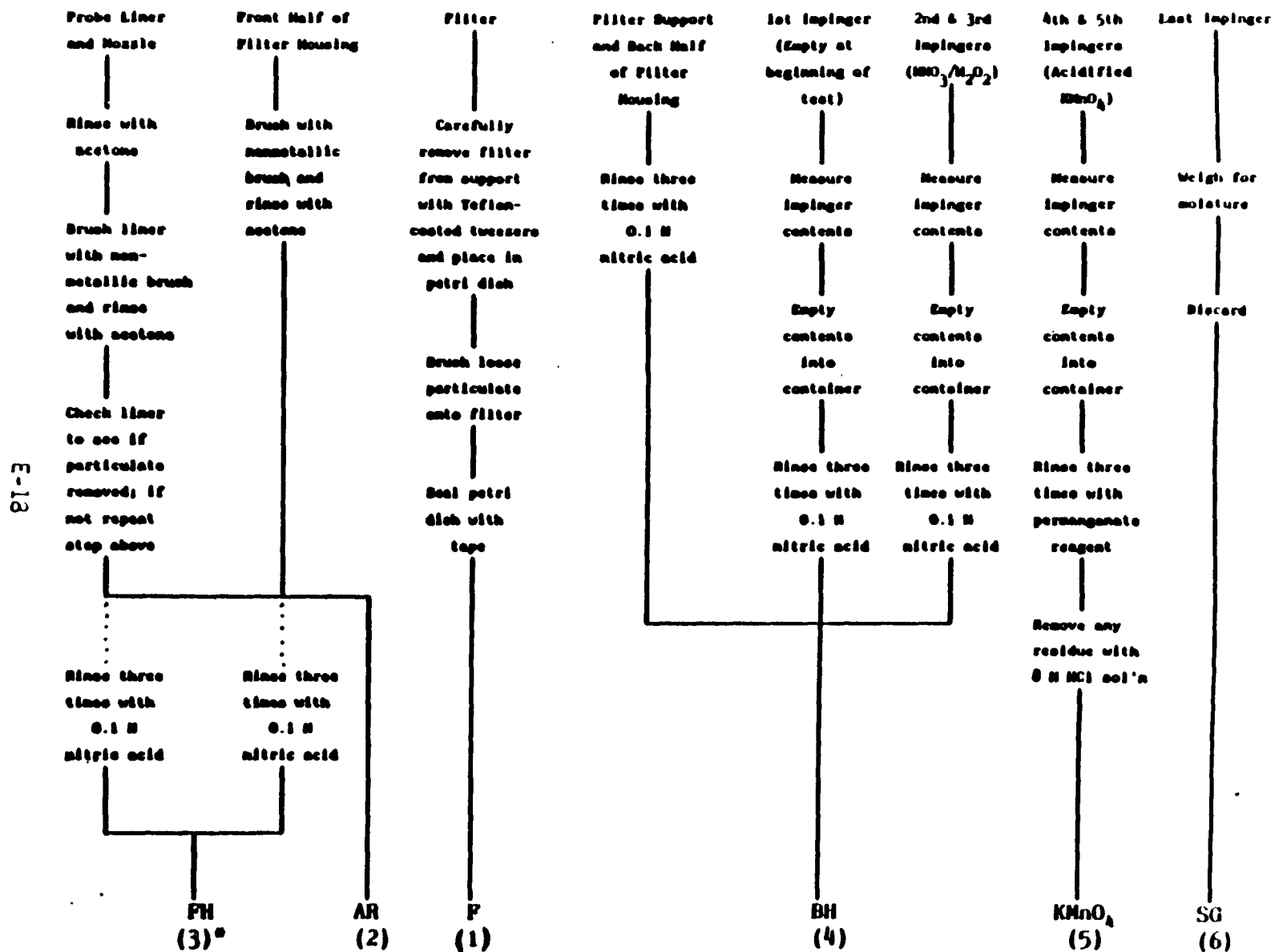
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or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. The sample is recovered and treated as follows (see schematic in Figure A-2). Assure that all items necessary for recovery of the sample do not contaminate it.

5.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water should be used to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

5.2.2 Container No. 2 (Acetone Rinse). Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 100 ml of acetone and placing the wash in a glass container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nonmetallic brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a nonmetallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample

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Probe Liner
and Nozzle
|
Rinse with
acetone
|
Brush liner
with non-
metallic brush
and rinse
with acetone
|
Check liner
to see if
particulate
removed; if
not repeat
step above
|
Rinse three
times with
0.1 N
nitric acid

Front Half of
Filter Housing
|
Brush with
nonmetallic
brush and
rinse with
acetone
|
Rinse three
times with
0.1 N
nitric acid

Filter
|
Carefully
remove filter
from support
with Teflon-
coated tweezers
and place in
petri dish
|
Brush loose
particulate
onto filter
|
Seal petri
dish with
tape

Filter Support
and Back Half
of Filter
Housing
|
Rinse three
times with
0.1 N
nitric acid

1st Impinger
(Empty at
beginning of
test)
|
Measure
impinger
contents
|
Empty
contents
into
container
|
Rinse three
times with
0.1 N
nitric acid

2nd & 3rd
Impingers
(HNO_3/H_2O_2)
|
Measure
impinger
contents
|
Empty
contents
into
container
|
Rinse three
times with
0.1 N
nitric acid

4th & 5th
Impingers
(Acidified
$KMnO_4$)
|
Measure
impinger
contents
|
Empty
contents
into
container
|
Rinse three
times with
permanganate
reagent
|
Remove any
residue with
8 N HCl sol'n

Last Impinger
|
Weigh for
moisture
|
Discard

PH
(3)*   AR
(2)   F
(1)   BH
(4) $KMnO_4$
(5)   SG
(6)

* Number in parentheses indicates container number.

Figure A-2. Sample recovery scheme.

container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe three times-or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Clean the inside of the front half of the filter holder by rubbing the surfaces with a nonmetallic nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

5.2.3 Container No. 3 (Probe Rinse). Rinse the probe liner, probe nozzle, and front half of the filter holder thoroughly with 100 ml of 0.1 N nitric acid and place the wash into a sample storage container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Perform the rinses as described in Method 12, Section 5.2.2. Record the volume of the combined rinse. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water followed by acetone and discard these rinses.

5.2.4 Container No. 4 (Impingers 1 through 3, Contents and Rinses). Due to the large quantity of liquid involved, the tester may place the impinger solutions in more than one container. Measure the liquid in the first three impingers volumetrically to within 0.5 ml using a graduated cylinder. Record the volume of liquid present. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N nitric acid as

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described in Method 12, Section 5.2.4. Note: The use of exactly 100 ml of 0.1 N nitric acid rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Calculate the 0.1 N nitric acid rinse volume by difference. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

5.2.5 Container No. 5 (Acidified Potassium Permanganate Solution and Rinses, Impingers No. 4 & 5). Pour all the liquid from the permanganate impingers (fourth and fifth, if two permanganate impingers are used) into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Using 100 ml total of the acidified potassium permanganate solution, rinse the permanganate impinger(s) and connecting glass pieces a minimum of three times. Combine the rinses with the permanganate impinger solution. Finally, rinse the permanganate impinger(s) and connecting glassware with 50 ml of 8 N HCl to remove any residue. Note: The use of exactly 100 ml and 50 ml for the two rinses is necessary for the subsequent blank correction procedures. Place the combined rinses and impinger contents in a labeled glass storage bottle. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.2.2 and properly seal the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles should not be filled full and should be vented to relieve excess pressure. Venting is highly recommended. A No. 70-72 hole drilled in the container cap and Teflon liner has been found to allow adequate venting without loss of sample.

5.2.6 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations.

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Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

5.2.7 Container No. 7 (Acetone Blank). Once during each field test, place 100 ml of the acetone used in the sample recovery process into a labeled container for use in the front half field reagent blank. Seal the container.

5.2.8 Container No. 8 (0.1 N Nitric Acid Blank). Once during each field test, place 200 ml of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use in the front half and back half field reagent blanks. Seal the container.

5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Blank). Once during each field test, place 200 ml of the 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use in the back half field reagent blank. Seal the container.

5.2.10 Container No. 10 (Acidified Potassium Permanganate Blank). Once during each field test, place 300 ml of the acidified potassium permanganate solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back half field reagent blank for mercury analysis. Seal the container.
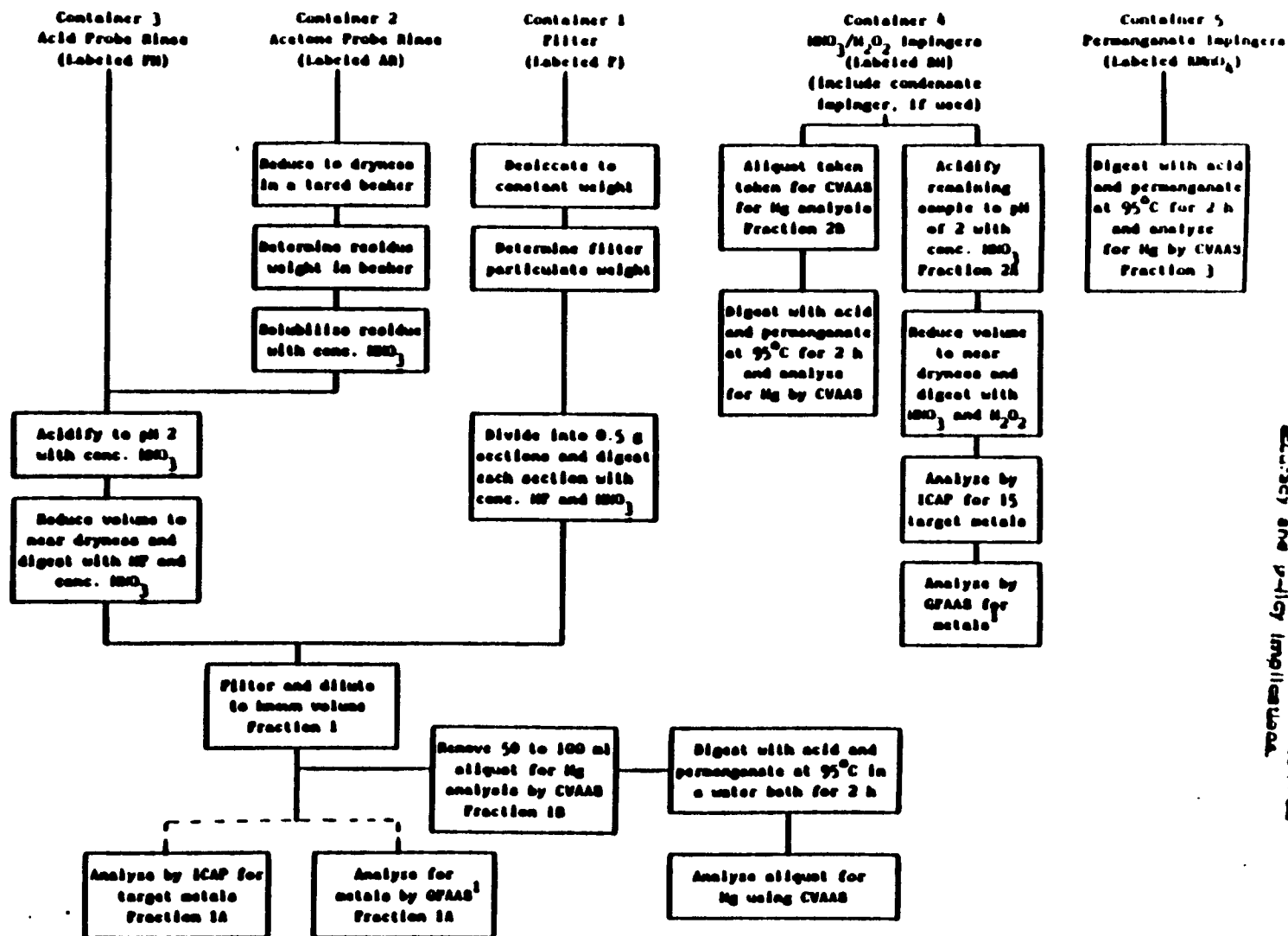
Note: This container should be vented, as described in Section 5.2.4, to relieve excess pressure.

5.2.11 Container No. 11 (8 N HCl Blank). Once during each field test, place 50 ml of the 8 N hydrochloric acid used to rinse the acidified potassium permanganate impingers into a labeled container for use in the back half reagent blank for mercury.

5.2.12 Container No. 12 (Filter Blank). Once during each field test, place an unused filter from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. This will be used in the front half field reagent blank.

5.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure A-3.

5.3.1 Container No. 1 (Filter). If particulate emissions are being determined, then desiccate the filter and filter catch without heat and weigh to

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Container 3
Acid Probe Rinse
(Labeled PR)

Container 2
Acetone Probe Rinse
(Labeled AR)

Container 1
Filter
(Labeled F)

Container 4
HNO_3/H_2O_2 Impingers
(Labeled BM)
(include condensate
impinger, if used)

Container 5
Permanganate Impingers
(Labeled MnO_4)

Reduce to dryness
in a tared beaker

Desiccate to
constant weight

Aliquot taken
taken for CVAAS
for Hg analysis
Fraction 2B

Acidify
remaining
sample to pH
of 2 with
conc. HNO_3
Fraction 2A

Digest with acid
and permanganate
at 95°C for 2 h
and analyze
for Hg by CVAAS
Fraction 3

Determine residue
weight in beaker

Determine filter
particulate weight

Solubilize residue
with conc. HNO_3

Digest with acid
and permanganate
at 95°C for 2 h
and analyze
for Hg by CVAAS

Reduce volume
to near
dryness and
digest with
HNO_3 and H_2O_2

Acidify to pH 2
with conc. HNO_3

Divide into 0.5 g
sections and digest
each section with
conc. HF and HNO_3

Analyze by
ICAP for 15
target metals

Reduce volume to
near dryness and
digest with HF and
conc. HNO_3

Analyze by
GFAAS for
metals[1]

Filter and dilute
to known volume
Fraction 1

Remove 50 to 100 ml
aliquot for Hg
analysis by CVAAS
Fraction 1B

Digest with acid and
permanganate at 95°C in
a water bath for 2 h

Analyze by ICAP for
target metals
Fraction 1A

Analyze for
metals by GFAAS[1]
Fraction 1A

Analyze aliquot for
Hg using CVAAS

[1]Analysis by AAS for metals found at less than 2 ug/ml in digestate solution, if desired. Or analyze for each metal by AAS, if desired.

Figure A-3. Sample preparation and analysis scheme.

a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual microwave pressure relief vessels or Parr° Bombs. Add 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12-15 minutes in intervals of 1 to 2 minutes at 600 Watts. For conventional heating, heat the Parr Bombs at 140°C (285°F) for 6 hours. Then cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 5.3.3, below.

Notes: 1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Twelve to 15 minute heating times have been found to be acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by sorbent reflux within the vessel.

2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to an acid-cleaned tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Resolubilize the residue with concentrated nitric acid and combine the resultant sample including all liquid and any particulate matter with Container No. 3 prior to beginning the following Section 5.3.3.

5.3.3 Container No. 3 (Probe Rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified with concentrated nitric acid to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 50 ml by heating on a hot plate at a temperature

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just below boiling. Inspect the sample for visible particulate matter, and depending on the results of the inspection, perform one of the following. If no particulate matter is observed, combine the sample directly with the acid digested portions of the filter prepared previously in Section 5.3 1. If particulate matter is observed, digest the sample in microwave vessels or Parr Bombs following the procedures described in Section 5.3.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1. The resultant combined sample is referred to as Fraction 1. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. Measure and record the combined volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 50 ml aliquot and label as Fraction 1B. Label the remaining 250 ml portion as Fraction 1A. Fraction 1A is used for ICAP or AAS analysis. Fraction 1B is used for the determination of front half mercury.

5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove a 50 ml aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as Fraction 2A. The Fraction 2B aliquot should be prepared and analyzed as described in Section 5.4.3. Fraction 2A shall be pH 2 or lower. If necessary, use concentrated nitric acid to lower Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in Sections 5.3.4.1 and 5.3.4.2, below.

5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent hydrogen peroxide and heat for 10 more minutes. Add 50 ml of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water.

5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent nitric acid and heat for 6 minutes in intervals of 1 to 2 minutes at 600 Watts. Allow the sample to cool. Add 10 ml of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 ml of hot water and heat for an additional 5 minutes.

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Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water.

Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

5.3.5 Container No. 5 (Impingers 4 & 5). Measure and record the total volume of this sample to within 0.5 ml. This sample is referred to as Fraction 3. Follow the analysis procedures described in Section 5.4.3.

5.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

5.4 Sample Analysis. For each sampling train, five individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure A-3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front half of the train. Fraction 1A is for ICAP or AAS analysis as described in Sections 5.4.1 and/or 5.4.2. Fraction 1B is for determination of front half mercury as described in Section 5.4.3.

The back half of the train was used to prepare the third through fifth samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the H_2O and HNO_3/H_2O_2 Impingers 1 through 3. Fraction 2A is for ICAP or AAS analysis. Fraction 2B will be analyzed for mercury.

The fifth sample, labeled Fraction 3, consists of the impinger contents and rinses from the permanganate Impingers 4 and 5. This sample is analyzed for mercury as described in Section 5.4.3. The total back half mercury catch is determined from the sum of Fraction 2B and Fraction 3.

5.4.1 ICAP Analysis. Fraction 1A and Fraction 2A are analyzed by ICAP using EPA Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 200.7. The quality control procedures described in Section 7.3.1 of this method shall be followed. Recommended wavelengths for use in the analysis are listed below.

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Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

Initially, analyze all samples for the target metals plus iron and aluminum. If iron and aluminum are present in the sample, the sample may have to be diluted so that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic and lead.

Note: When analyzing samples in a hydrofluoric acid matrix, an alumina torch should be used; since all front half samples will contain hydrofluoric acid, use an alumina torch.

5.4.2 AAS by Direct Aspiration and/or Graphite Furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AAS is desired, Table A-2 should be used to determine which techniques and methods should be applied for each target metal. Table A-2 should also be consulted to determine possible interferences and techniques to be followed for their minimization. Calibrate the instrument according to Section 6.3 and follow the quality control procedures specified in Section 7.3.2.

5.4.3 Cold Vapor AAS Mercury Analysis. Fraction 1B, Fraction 2B, and Fraction 3 should be analyzed for mercury using cold vapor atomic absorption spectroscopy following the method outlined in EPA Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F. Set up

TABLE A-2. APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTEFERENCE FOR AAS ANALYSIS

Metal	Technique	Method No.	Wavelength (nm)	Interference Cause	Minimization
Sb	Aspiration	7040	217.6	1000 mg/ml Pb Ni, Cu, or acid	Use secondary wavelenght of 231.1 nm. Match sample & standards acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
As	Furnace	7060	193.7	Arsenic volati - zation Aluminium	Spiked samples & add nickel nitrate solution to digestates prior to analyses Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium Barium ionization	High hollow cathode current & narrow band set 2 mL of KCl per 100 mL of sample
Be	Aspiration	7090	234.9	500 ppm Al High Mg & Si	Add 0.1% fluoride Use method of standard additions
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects
Cd	Aspiration	7130	228.8	Absorption & light scattering	Background correction is required
Cd	Furnace	7131	228.8	As above Excess chloride Pipet tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips
Cr	Aspiration	7190	357.9	Alkali metal Absorption & scatt	KCl ionization suppressant in sample & stand Consult manufacturer's literature
Cr	Furnace	7191	357.9	200 mg/L calcium & phosphate	All calcium nitrate for a know constant effect and to eliminate effect of phosphate

(continued)

Metal	Technique	Method No.	Wavelength (nm)	Interference Cause	Minimization
Cu	Aspiration	7210	324.7	Absorpt. & scatter	Consult manufacturer's manual
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternat	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 ul. of phosphorus acid to 1-ml. of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternat	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternat Fe, Co, & Cr Nonlinear respons	Background correction required Matrix matching or a nitrous-oxide/acety flame Sample dilution or use .352.4 nm line
Se	Furnace	7740	196.0	Volitality Adsorpt. & scatter	Spike samples & reference materials & add nickel nitrate to minimize volatilization Background correction is required & Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Absorpt. & scatter AgCl insoluble Viscosity	Background correction is required Avoid hydrochloric acid unless silver is in solution as a chloride complex Sample & standards monitored for apiration rate
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required Verify that losses are not occuring for volitization by spiked samples or standad addt Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu & P Contamination	Strontium removes Cu and phosphate Care should be taken to avid contamination